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Attorney Docket No. 2950.08US02

APPEAL BRIEF TRANSMITTAL

In re the application of:

Reitz et al.
Application No.: 09/266,202
Filed: March 10, 1999
For: ZINC OXIDE PARTICLES

Confirmation No.: 5465
Examiner: K. S. Lee
Group Art Unit: 2832

Mail Stop Appeal Brief-Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Transmitted herewith is the Second Corrected Appeal Brief (14 pages plus Appendices 1-3) in the above-identified application, with respect to the Notice of Appeal filed on August 17, 2004. The Corrected Appeal Brief addresses issues raised in the Notification of Non-Compliant Appeal Brief we mailed April 7, 2005. The fee for filing the Appeal Brief was previously filed in this case such that no additional fees are due.

Respectfully submitted,

Peter S. Dardi, Ph.D.
Registration No. 39,650

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 16-0631.

CERTIFICATE OF MAILING

I hereby certify that this document is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on

April 14, 2005
Date of Deposit

Peter S. Dardi

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Application Number 09/266,202

PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Attorney Docket No.: 2950.08US02

Reitz et al.

Confirmation No.: 5465

Application No.: 09/266,202

Examiner: K. S. Lee

Filed: March 10, 1999

Group Art Unit: 2832

For: ZINC OXIDE PARTICLES

RESPONSE TO NOTIFICATION OF NON-COMPLIANT APPEAL BRIEF

Mail Stop Appeal Brief-Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

In response to the Notification of April 7, 2005, Appellants file herewith a Second Corrected Appeal Brief. Appellants note that all of the issues raised in the April 7, 2005 Office Action could all have been raised in a January 12, 2005 Office Action regarding the first appeal brief filed.

Furthermore, three issues were raised in the Notification of April 7, 2005. The first related to the status of the claims. The only "error" Appellants could identify here was that the heading was "STATUS OF THE CLAIMS" rather than "STATUS OF CLAIMS." Appellants further clarified that all of the rejected claims were appealed, but this was already indicated in the introduction of the Brief and was obvious in context.

The second issue related to the statement of grounds of rejection appealed. Here, Appellants had used the older heading of "ISSUES" rather than "GROUND OF REJECTION TO BE REVIEWED ON APPEAL." But the rules do not require a particular heading but only an "appropriate heading." 37 C.R.F. 41.37(c)(1). Especially given that the Office did not note this in the January 12, 2005 Office Action, no explanation was presented why Appellants' heading was not appropriate. The heading was amended in the Second Correct Appeal Brief.

Finally, the Notification of April 7, 2005 indicated that a decision in a related appeal was not attached. Appellants had noted that the issues in the two cases were unrelated since they do not involve the same art at all. Nevertheless, the second corrected appeal brief has the decision attached.

Respectfully submitted,



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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Attorney Docket No.: 2950.08US02

Reitz et al.

Confirmation No.: 5465

Application No.: 09/266,202

Examiner: K. S. Lee

Filed: March 10, 1999

Group Art Unit: 2832

For: ZINC OXIDE PARTICLES

BEFORE THE PATENT BOARD OF APPEALS AND INTERFERENCES

SECOND CORRECTED APPEAL BRIEF

Mail Stop Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This is an appeal from the Final Office Action dated April 21, 2004, in which claims 1-5, 7-9 and 25-30 were finally rejected. A Notice of Appeal was filed on August 17, 2004. This Corrected Appeal Brief corrects issues raised in the Notice of Non-Compliant Amendment dated April 7, 2005. A separate response to this Office Action is filed herewith.

Please grant any extension of time necessary for entry; charge any fee due to Deposit Account No. 16-0631.

CERTIFICATE OF MAILING

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April 14, 2005
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REAL PARTY IN INTEREST

NanoGram Corporation, a corporation organized under the laws of the state of Delaware, and having offices at 2911 Zanker Road, San Jose, California, has acquired the entire right, title and interest in and to the invention, the application, and any and all patents to be obtained therefore, as per the Assignment, recorded at Reel 010198, Frame 0778 from the inventors to NeoPhotonics Corporation and an assignment from NeoPhotonics Corporation to NanoGram Corporation, recorded at Reel 013957, Frame 0076. Note that NeoPhotonics Corporation was formerly called NanoGram Corporation, and the present NanoGram Corporation was previously a wholly owned subsidiary of NeoPhotonics Corporation following the formal name change. The present NanoGram Corporation is now an independent corporation, but affiliated with the earlier NanoGram Corporation, now named NeoPhotonics Corporation.

RELATED APPEALS AND INTERFERENCES

The parent case 08/962,362 filed on October 3, 1997 was the subject of an earlier appeal. Specifically, Application 08/962,362 was subject of Appeal 2001-2242, decision of which is attached as Appendix 3. This earlier decision is attached even though the issues are not directly related. The parent case was recently appealed for a second time, but the parent case has re-enter prosecution and is not presently on appeal. A child case 09/970,279 filed on October 2, 2001 is presently under appeal, but none of the issues in the two cases overlap. The child application 09/970,279 is directed to apparatuses with multiple inlet nozzles.

STATUS OF CLAIMS

Claims 1-5, 7-9 and 25-30 are pending and stand rejected. All of the rejectioned claims are presently appealed. Claims 6, 10-24 and 31-40 have been canceled. The pending claims are listed in Appendix 1.

STATUS OF AMENDMENTS

All amendments have been entered.

SUMMARY OF THE INVENTION

The present invention relates to highly uniform collections of nanoscale crystalline zinc oxide particles. Several forms of zinc oxide are described. An embodiment of the improved zinc oxide particles are shown in a micrograph in Fig. 16, which does not make use of reference numbers on the photograph according to standard convention since the particles are clearly identifiable.

The method of production claims from the application as filed were restricted out from the present application. These method claims were directed to a laser pyrolysis approach for the generation of zinc oxide. Laser pyrolysis can be very effective at the production of highly uniform particles due to a highly localized reaction zone. In particular, the reaction is rapidly quenched as the flow leaves the light beam. Laser pyrolysis is described throughout the Appellants' specification. In particular, see page 6, line 20 to page 8, line 13 and the Example as well as suitable apparatuses for performing the method in Figs. 1-8.

An example of particle size distribution is plotted in Fig. 17 for the zinc oxide particles described in the example. In general, the uniformity of the zinc oxide particles is claimed based on two distinct ways of describing the uniformity. In claim 1, the uniformity is described based on the drop off of the distribution away from the average particle diameter. To put the description in reverse, less than 5 percent of the particles have a diameter greater than about 160 percent of the average particle diameter, and less than 5 percent of the particles have a diameter less than about 40 percent of the average diameter. These conditions indicate that the particle size distribution is

sharply peaked near the average diameter and specify the criteria to evaluate if it is sharply peaked enough to fall within the claims.

The second way to specify the uniformity is the subject of claims 4, 5, and 25. As this is sometimes put, there are no "boulders." In the nano-world, a boulder is of course very small. More specifically, in these claims the particle size distribution is described as lacking a tail in the distribution at larger diameters. Thus, the distribution is cut off abruptly with a specific cut-off in diameter specified in the claims. This feature is very difficult to achieve since most approaches for forming particles involve a chemical equilibrium with a corresponding distribution that drops off gradually. The laser pyrolysis process is inherently a non-equilibrium process and does not have these limitations. Only a very few other approaches are able to form a very limited number of other inorganic particles with this lack of a tail. Other approaches have not been known to form such uniform zinc oxide. The properties of the particles are described further in the specification, for example, at page 32, line 34 to page 36, line 7.

Claims 7-9 and 30 are directed to the use of the zinc oxide in resistors, varistors and specific forms thereof. Applicants' specification describes these electrical components, for example, at page 40, lines 17 to page 41, line 3.

GROUND OF REJECTION TO BE REVIEWED ON APPEAL

1. Whether claims 1-5, 7-9 and 25-30 are anticipated by U.S. Patent 6,200,680 to Takeda et al.?

GROUPING OF CLAIMS

This section is not required by the rules and is included for the convenience of the Board with respect to evaluating the analysis below.

Claims 1-3, 27 and 29 are within a first claim group directed to a uniform collection of crystalline zinc oxide particles.

Claims 4, 5 and 25 are within a second claim group directed to uniform collections of crystalline zinc oxide particles with no large particles.

Claims 7, 8 and 9 are within a third group of claims directed to resistors elements comprising collections of crystalline zinc oxide particles.

Claim 26 is within a fourth claim group directed to a varistor with non-linear voltage dependence.

Claim 28 is within a fifth claim group directed to a collection of particles that are not elongated.

Claim 30 is within a sixth claim group directed to a collection of particles comprising ZnO₂.

ARGUMENT

The Examiner rejected claims 1-5, 7-9 and 25-30 under 35 U.S.C. § 102(e) as being anticipated by U.S. Patent 6,200,680 to Takeda et al. (the Takeda patent). A copy of the Takeda patent is found in Appendix 2. The Examiner asserted that the Takeda patent explicitly or inherently disclosed all of the features of Applicants' claimed invention. Appellants maintain strenuously that the Examiner has fallen far short of establishing prima facie anticipation of any of Appellants' claims. Appellants respectfully request reconsideration of the rejections based on the following arguments.

A. Legal Background

1. Burden of Persuasion

The Examiner has the burden of establishing a prima facie case of anticipation. As such, the Examiner must provide a reference that discloses every element as set forth in the claim. "A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference." Verdegaal Bros. v. Union Oil Co. of California, 814 F2d. 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987) (MPEP §2131).

2. A Single Reference Must Identically Disclose Every Element Set Forth In a Claim To Anticipate The Claim

"In order to constitute anticipatory prior art, a reference must identically disclose the claimed compound..." MPEP 2122 citing In re Schoenwald, 22 USPQ2d 1671, (Fed. Cir. 1992). "For a prior art reference to anticipate in terms of 35 U.S.C. § 102, **every element of the claimed invention must be identically shown in a single reference**. These elements must be arranged as in the claim under review, but this is not an 'ipsissimis verbis' test." In re Bond, 15 USPQ2d 1566, 1567 (Fed. Cir, 1990)(Internal citations omitted and emphasis added.).

"If the prior art reference does not expressly set forth a particular element of the claim, that reference still may anticipate if that element is 'inherent' in its disclosure. To establish inherency, the intrinsic evidence 'must make it clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill. Inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient.'" In re Robertson, 49 USPQ2d 1949, 1950, 1951 (Fed. Cir. 1999), citing Continental Can Co. v. Monsanto Co., 20 USPQ2d 1746, 1749 (Fed. Cir. 1991).

"Every element of the claimed invention must be literally present, arranged as in the claim. **The identical invention must be shown in as complete detail as is contained in the patent claim.**" Richardson v. U.S. Suzuki Motor Corp., 9 USPQ2d 1913, 1920 (Fed. Cir. 1989)(Internal citations omitted, and emphasis added.); see also MPEP 2131. "Here, as well, anticipation is **not** shown by a prior art disclosure which is only 'substantially the same' as the claimed invention." Jamesbury Corp. v. Litton Industrial Products, Inc., 225 USPQ 253, 256 (Fed. Cir. 1985)(emphasis added).

Similar requirements also hold under an obviousness rejection. Prima facie obviousness is not established if all the elements of the rejected claim are not disclosed or suggested in the cited art. In re Ochiai, 37 USPQ 1127, 1131 (Fed. Cir. 1995). ("The test for obviousness *vel non* is statutory. It requires that one compare the claim's 'subject matter as a whole' with the prior art 'to which said

subject matter pertains.""). See also, MPEP 2143.03 "All Claim Limitations Must Be Taught or Suggested," citing In re Royka, 180 USPQ 580 (CCPA 1974). "To establish prima facie obviousness of a claimed invention, all of the claim limitations must be taught or suggested by the prior art." MPEP 2143.03.

3. Compositions Of Matter

It is long established that a composition of matter is indistinguishable from its properties. In re Papesch, 137 USPQ 43, 51 (CCPA 1963); In re Cescon, 177 USPQ 264, 266 (CCPA 1973). There are two types of properties, chemical/compositional properties and physical properties. The chemical/compositional properties of the composition of matter determine what the material is, while the physical properties relate to the interaction and behavior of the composition of matter. Often unique or unexpected physical properties are used to establish the existence of an unobvious composition when chemical/compositional properties either are unknown or do not fully represent the unobviousness of the composition. However, discovery of a surprising or unexpected physical property does not necessarily control an obviousness determination, and all the evidence under the Graham factors must be considered. See, for example, Richardson-Vicks v. Upjohn Co., 44 USPQ2d 1181, 1187 (Fed. Cir. 1997). **In the present case, the claims do not relate to the discovery of properties of previously known or suggested materials.**

These issues regarding properties of compositions of matter were considered explicitly in the context of **chemical powders** in In re Grose, 201 USPQ 57 (CCPA 1979). The specific issue in the Grose case was the crystal structure of zeolites in a collection of zeolite particles. **Crystal structure, like particle size distribution or chemical formula, is a chemical/ compositional property of the composition of matter.** The zeolites in the Gross case were collections of particles, i.e., a powder. The relevant issues are well stated in In re Grose:

Though nonobviousness of appellants' process for preparing their claimed composition would not be determinative of nonobviousness of the composition, a

holding that the composition would have been nonobvious would require that the prior art fail to disclose or render obvious a process for preparing it.

[I]f the prior art of record fails to disclose or render obvious a method for making a claimed compound, at the time the invention was made, it may not be legally concluded that the compound itself is in the possession of the public. In this context, we say that the absence of a known or obvious process for making the claimed compounds overcomes a presumption that the compounds are obvious. ***

In re Hocksema, 55 CCPA 1493, 1500, 399 F.2d 269, 274, 158 USPQ 596, 601 (1968)(foot note omitted). Failure of the prior art to disclose or render obvious a method for making any composition of matter, whether a compound or a mixture of compounds like a zeolite, precludes a conclusion that the compound would have been obvious.

In re Grose, 201 USPQ at 63-64 (emphasis added). Applicants note that in In re Grose the zeolites had the same chemical formula as the prior art zeolites and only differed in crystal structure.

Another CCPA case similarly ruled that an anhydrous crystalline form of a material was patentable over a non-crystalline form. In re Irani, 166 USPQ 24 (CCPA 1970). As stated in that case,

As stated above, even assuming that one skilled in the art could have predicted with reasonable certainty that crystalline anhydrous ATMP could be produced, we are not convinced by this record how this could be achieved. We note that neither the examiner nor the board has contended that a suitable process would have been obvious. The closest that either has come to such a contention is the examiner's statement based on the disclosure in the Irani patent, that, as it turns out, 'little modification of the Petrov *** process will produce a crystalline material.' Obviousness, however, must not be based on hindsight and a 'little modification' can be a most unobvious one.

In view of the foregoing, we need not consider appellants' arguments regarding the differences in properties between appellants and Petrov's forms of ATMP.

In re Irani, 166 USPQ at 27 (bold added).

4. To Support A Finding Of Unpatentability Based On Cited Art, The Cited Art Must Provide A Means Of Obtaining The Claimed Composition Or Apparatus

The proposition is well established that the cited art only renders a composition of matter or

apparatus unpatentable to the extent that the cited art enables the disputed claims, in other words, if the cited art provides a means of obtaining the claimed composition or apparatus.

To the extent that anyone may draw an inference from the Von Bramer case that the mere printed conception or the mere printed contemplation which constitutes the designation of a 'compound' is sufficient to show that such a compound is old, regardless of whether the compound is involved in a 35 U.S.C. 102 or 35 U.S.C. 103 rejection, we totally disagree. ... We think, rather, that the true test of any prior art relied upon to show or suggest that a chemical compound is old, is whether the prior art is such as to place the disclosed 'compound' in the possession of the public. In re Brown, 141 USPQ 245, 248-49 (CCPA 1964)(emphasis in original)(citations omitted).

Similarly, see In re Hoeksema, 158 USPQ 596, 600 (CCPA 1968)(emphasis in original):

We are certain, however, that the invention as a whole is the claimed compound and a way to produce it, wherefore appellant's argument has substance. There has been no showing by the Patent Office in this record that the claimed compound can exist because there is no showing of a known or obvious way to manufacture it; hence, it seems to us that the 'invention as a whole,' which section 103 demands that we consider, is not obvious from the prior art of record.

While there are valid reasons based on public policy as to why this defect in the prior art precludes a finding of obviousness under section 103, In re Brown, supra, its immediate significance in the present inquiry is that it poses yet another difference between the claimed invention and the prior art which must be considered in the context of section 103. So considered, we think the differences between appellant's invention as a whole and the prior art are such that the claimed invention would not be obvious within the contemplation of 35 U.S.C. 103.

The Federal Circuit has further emphasized these issues. "But to be prior art under section 102(b), a reference must be enabling. That is, it must put the claimed invention in the hands of one skilled in the art." In re Sun, 31 USPQ2d 1451, 1453 (Fed. Cir. 1993)(unpublished). Assertions in a prior art reference do not support an anticipation or obviousness rejection unless the references place the claimed invention in the hands of the public. Beckman Instruments Inc. v. LKB Produkter AB, 13 USPQ2d 1301, 1304 (Fed. Cir. 1989). "In order to render a claimed apparatus or method obvious, the prior art must enable one skilled in the art to make and use the apparatus or method."

Id. While a properly citable reference is prior art for all that it teaches, references along with the knowledge of a person of ordinary skill in the art must be enabling to place the invention in the hands of the public. In re Paulsen, 31 USPQ2d 1671, 1675 (Fed. Cir. 1994). See also In re Donohue, 226 USPQ 619, 621 (Fed. Cir. 1985).

B. Analysis - Rejection Over Takeda et al.

The Examiner asserted that the claims met the particle size limitations as well as the distribution of particle sizes. The Examiner further asserted that the Takeda patent disclosed particles with a diameter of "about 5 nm." Furthermore, The Examiner asserted that the Takeda reference inherently discloses a varister and teaches the stoichiometry of zinc oxide. In addition, the Examiner asserted that the Takeda patent disclosed a white metal oxide comprising antimony. With all due respect, Applicants maintain that the Examiner has fallen far short of establishing prima facie anticipation for the reasons described in the following.

1. Group 1 Claims

Scope of Claim 1

In an Advisory Action dated September 29, 2004, the Examiner stated "The fine particles meet the claims before and after being formed into a composition. As for the latter, Applicants' claim does not preclude other elements." This statements suggests that the Examiner is taking an inappropriate meaning for the term particle.

First, an article should be scrutinized based on what it is and not based on how it is formed or what its components could be. With respect to the Takeda patent, the fine powders are used to form composite particles. The composite particles are not still fine particles, and similarly a car is not steel ingots. From that perspective, one must separately examine the composite particles or the fine particles to see if they anticipate Appellants' claimed invention.

It is definitely true that Appellants' claims do not preclude other elements. Thus, from a composition point of view alone, the composite particles may possibly meet the feature relating

to crystalline zinc oxide composition. However, the composite particles do not meet the other features of Appellants' claimed invention as explained in detail below. Similarly, the fine particles do not meet all of the claim features as described in detail below. However, before completing the analysis, the meaning of the term particle is considered.

The plain and clear meaning of a particle in this context is a separate entity that can be identified distinct from other particles. However, in the material community, the term primary particle is sometimes used to refer to particles that are formed as intermediates in the synthesis process but are fused into the ultimate particles. Since the ultimate particles may have properties that reflect the intermediates it can be convenient to refer to primary particle size as a property of the ultimate or secondary particles. If the process used to form the particles does not produce intermediate particles, the primary particles and secondary particles are the same. Nevertheless, as disclosed and claimed by Appellants it is clear that the claim term particle is referring to physical particles or secondary particles, and not to fused primary particles. This is the ordinary meaning, and there is no reason from Appellants' specification to give the term a different meaning.

Analysis of Group 1 Claims

The Takeda patent discloses two materials that could but do not fall under Applicants' claims. One of these materials is referred to as a fine powder and the second material is a composite. The relationship of these materials is described schematically in a diagram in Appendix C. Specifically, the fine particles are incorporated into the composite particles.

The composite particles are easy to distinguish over Applicants' claimed compositions of matter. The composite particles can comprise crystalline zinc oxide. However, the composite particles have average particle sizes of 0.1 to 10 microns. See, for example, column 25, lines 29-30. It is not clear whether or not the uniformity specified in the Takeda patent for the composite particles falls within Applicants' claimed uniformity. But this is irrelevant since the composite particles do not have the claimed average particle size. Specifically, about 95 nanometers is less

than 100 nanometers or 0.1 microns. Therefore, the composite particles clearly do not anticipate Applicants' claimed invention.

The Examiner asserted in the Advisory Action of September 9, 2004, that the fine particles anticipate before incorporation into the composite particles. Unfortunately, the Examiner has never explained the basis for this position. Under the clear law, the Examiner has the burden of establishing prima facie anticipation by showing that all the claim limitations are found in a single reference and arranged as in the claim. The Examiner has failed to do this. Nevertheless, while Appellants have no obligation to do this, Appellants will explain why the fines do not meet the claim limitations, to advance prosecution of the case.

As Appellants have repeatedly pointed out, the Takeda patent does not teach the claimed uniformity for the zinc oxide fines. With respect to the process for make zinc oxide, Example 14 described the formation of large agglomerates. These agglomerates are pulverized to make the fines. Referring to Fig. 2 and the discussion in column 89, lines 11-21, it is clear that the fines are primary particles that are agglomerated. The fragments in Fig. 2 are just that fragments. The resulting "particles" seen in Fig. 2 are in a wide range of shapes and sizes consistent with the particles being fragments. These fines in no way have a uniformity close to the uniformity disclosed and claimed by Appellants. Therefore, the fine zinc oxide particles clearly do not come close to rendering Appellants' claims prima facie anticipated.

The Examiner has clearly fallen far short of establishing prima facie anticipation. Claims 1-3, 27 and 29 are not anticipated by the Takeda patent.

Group 2 Claims

Claims 4, 5 and 25 specify the uniformity with respect to the lack of particles with especially large diameters. As discussed above, the Takeda particles are formed by grinding which results in a wide range of particle sizes. Since grinding is an imprecise process, there will remain some ineffectively ground particles. Thus, the resulting particles will not lack especially large particles. Therefore, these claims are clearly not anticipated, and the Examiner has clearly failed to establish prima facie anticipation.

Group 3 Claims

Group 3 claims are directed to a resistor, varistor and a varistor with a non-linear voltage dependence. The Takeda patent does not discuss any of these devices. The Examiner asserts that the Takeda patent inherently discloses these devices. The only possible basis for this assertion is that the powder or generic structures formed from the powder is basically a resistor. According to the Webster's 10th Collegiate Dictionary, a resistor is "a device that has electrical resistance and that is used in an electrical circuit for protection, operation, or current control." Applicants specification shows one embodiment with electrical leads. While this is not the only embodiment of a resistor certainly, the Examiner has not pointed to any structure in the Takeda patent that **necessarily** (as required by law) could be incorporated as is into an electrical circuit. Therefore, the Examiner clearly has fallen far short of establishing prima facie anticipation.

Group 4 Claims

Claim 26 indicated that 95% of the particle are not rod shaped in that they have an aspect ratio less than two. Referring to Fig. 2, the prominent particle in the view has a length of roughly 8.5 centimeters and a width of about 5.5 centimeters. Presumably, the magnification is not distorting the shape of the particles. While the aspect ration of this one particle is less than two, about 1.55, it seems unlikely that these fragments will have less than 5 percent of the particles with an aspect ratio less than 2. In any case, the Examiner has not asserted how this condition is met by the particles in the Takeda patent. Therefore, the Examiner has clearly failed to assert a case of prima facie anticipation of claim 26 over the Takeda patent.

Group 5 Claim

Claim 28 specifies that the zinc oxide has a stoichiometry of ZnO_2 . The Takeda patent indicates only a stoichiometry of ZnO . The Examiner indicated that the reference "teaches the stoichiometry of zinc oxide." Perhaps ZnO , but not ZnO_2 . Since the reference falls far far short of disclosing identically the claimed invention, the Takeda patent clearly does not anticipate Applicants' claimed invention, and the Examiner has failed to assert a case of prima faice anticipation.

Group 6 Claim

Claim 30 indicates an electrical resistor further comprising a metal/metalloid oxide selected from a particular group. As noted above, the Takeda patent does not disclose an electrical resistor structure. The Examiner points to the disclosure of a white metal oxide, but the Examiner does not point to the white metal oxide within an electrical resistor. Again, the Examiner has fallen far-far short of establishing prima facie anticipation.

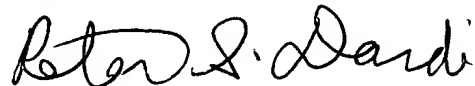
Summary

The Examiner has failed to assert a prima facie case of anticipation for any of the claims. Appellants have further explained why the Takeda patent clearly does not render Applicants' claimed invention anticipated.

CONCLUSIONS

Applicants submit that claims 1-5, 7-9 and 25-30 are free of the Takeda patent. Applicants believe that the Patent Office has failed to meet their burden of persuasion with respect to unpatentability of any of the claims on the present record. Thus, Applicants Respectfully request the reversal of the rejections of claims 1-5, 7-9 and 25-30 and allowance of the application.

Respectfully submitted,



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APPENDIX 1

1. A collection of particles in a powder comprising crystalline zinc oxide, the collection of particles having an average diameter less than about 95 nm and a distribution of particle sizes such that at least 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.
2. The collection of particles of claim 1 wherein the collection of particles have an average diameter less than about 45 nm.
3. The collection of particles of claim 1 wherein the collection of particles have an average diameter from about 5 nm to about 25 nm.
4. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about four times the average diameter of the collection of particles.
5. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about three times the average diameter of the collection of particles.
6. (Cancelled)
7. An electrical resistor component comprising the collection of particle of claim 1.
8. The electrical resistor component of claim 7 wherein the component is a varister.
9. The electrical resistor component of claim 8 wherein the varister has a non-linear voltage dependence.

10-24. (Cancelled)

25. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about two times the average diameter of the collection of particles.

26. The collection of particles of claim 1 wherein at least 95 percent of the particles have ratios of the dimension along the major axis to the dimension along the minor axis less than about 2.

27. The collection of particles of claim 1 wherein the zinc oxide has a stoichiometry of ZnO .

28. The collection of particles of claim 1 wherein the zinc oxide has a stoichiometry of ZnO_2 .

29. The collection of particles of claim 1 wherein the zinc oxide has a Zincite crystal structure.

30. The electrical resistor component of claim 7 further comprising metal/silicon oxide particles selected from the group consisting of Bi_2O_3 , Sb_2O_3 , SiO_2 , Co_2O_3 , and MnO_2 .

31-40. (Cancelled)



2950. 08/US-01

The opinion in support of the decision being entered today was not written for publication and is not binding precedent of the Board.

RECEIVED

MAR 24 2003

PATTERSON, THUENTE, SKAAR
& CHRISTENSEN, P.A.

Paper No. 30

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES

DOCKETED

Ex parte NOBUYUKI KAMBE
and XIANGXIN BI

MAILED

MAR 18 2003

Appeal No. 2001-2242
Application 08/962,362¹

PAT. & T.M. OFFICE
BOARD OF PATENT APPEALS
AND INTERFERENCES

ON BRIEF

Before JERRY SMITH, BARRETT, and RUGGIERO, Administrative Patent Judges.

BARRETT, Administrative Patent Judge.

DECISION ON APPEAL

This is a decision on appeal under 35 U.S.C. § 134 from the examiner's final rejection of claims 1-6 and 20-30, all the pending claims in the application.

We affirm.

¹ Application for patent filed October 31, 1997, entitled "Phosphors."

Request for Reconsideration

deadline 4-18-03;

Notice of Appeal to CAFC

deadline 5-18-03

BACKGROUND

The disclosed invention involves fluorescent particles with average dimensions of 5 to 100 nanometers (nm), called nanoparticles, which have a very uniform distribution of diameters. The fluorescent particles emit light in response to electrical stimulation. Therefore, the particles are suitable for incorporation into display devices wherein the particles are selectively excited to produce an image. The use of highly uniform particles provides for greater control over the emissions of the particles. Particles with a narrow particle size distribution have a corresponding light emission band covering a narrow frequency range (color). The uniformity of the particles leads to processing advantages with respect to the formation of thin layers with sharp edges. Nanoparticles with a very narrow particle size distribution are produced by a laser pyrolysis system described in the disclosure, but not claimed. These highly uniform particles are particularly well suited for the formation of improved display devices.

The following claim further illustrates the invention.

1. A display device comprising phosphor particles having an average diameter less than about 100 nm and wherein the phosphor particles comprise a collection of particles having a diameter distribution such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

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The examiner relies on the following references:

Jaskie	5,442,254	August 15, 1995
Bhargava	5,455,489	October 3, 1995

Claims 1, 4-6, 20-25 and 27-30 stand rejected under
35 U.S.C. § 103(a) as being unpatentable over Jaskie.

Claims 2, 3, and 26 stand rejected under 35 U.S.C. § 103(a)
as being unpatentable over Jaskie in view of Bhargava.

We refer to the final rejection (Paper No. 18) (pages
referred to as "FR__") and the examiner's answer (Paper No. 24)
(pages referred to as "EA__") for a statement of the examiner's
rejection, and to the appeal brief (Paper No. 23) (pages referred
to as "Br__") and the reply brief (Paper No. 25) (pages referred
to as ("RBr__") for a statement of appellants' arguments
thereagainst.

OPINION

Grouping of claims

The claims are argued to stand or fall together (Br5).
Therefore, for purposes of this appeal, the claims will stand or
fall together with claim 1.

The disclosed and claimed invention

Appellants describe a laser pyrolysis system for "the
production of particles with a highly uniform size distribution
and structural homogeneity" (spec. at 11, lines 19-20). The
"collection of particles has an average diameter ... preferably

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from about 5 nm to about 100 nm" (spec. at 18, lines 5-8). In addition, "the particles generally have a distribution of sizes such that at least 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter" (spec. at 19, lines 6-10). The specification describes that very small particle diameters allow for adjustment of emission characteristics without the need to activate the particles with a second metal (spec. at 20, lines 1-4) and that the particles may be phosphors (spec. at 21, lines 15-16).

Appellants seek to claim phosphor particles having a particular average size (i.e., "an average diameter less than about 100 nm" in claim 1) and uniformity (i.e., "about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter" in claim 1), the average diameter $\pm 60\%$, without claiming the method of producing the particles. The size and uniformity of the particles are said to result from the disclosed laser pyrolysis system; however, since the laser pyrolysis system is not claimed, particles having the claimed size and uniformity produced by any process will satisfy the claims.

It is apparently appellants' position (although not expressly stated) that they are entitled to broadly claim the particle size and uniformity limitations without claiming the

method of production because they were the first ones to come up with a method that allows production of particles having these uniformity characteristics.

The rejection over Jaskie

Jaskie discloses that the properties of quantum contained particles are designed chiefly by selecting the size (diameter) (col. 6, lines 39-41). It is disclosed that the color of the emitted light is adjusted, or tuned, by adjusting the size distribution of the particles during manufacture (col. 6, lines 43-46). It is disclosed that 50 Å (5 nm) diameter particles have a yellow to yellow orange color, reducing the size of the particles moves the emitted color to the blue end of the spectrum, and by increasing the size, the emitted color is moved toward the red end of the spectrum, with the maximum size being 100 Å (10 nm) (col. 6, lines 46-54). The particle materials provide luminescence (col. 5, lines 6-12) and are "phosphors," as claimed. Thus, Jaskie discloses quantum contained phosphor particle sizes approximately 10 times smaller than appellants' particle sizes and used for the same purpose.

Jaskie discloses two methods of manufacturing quantum contained particles, the micelle or inverse micelle technique and an etching technique (col. 6, line 62 to col. 7, line 27), and a method of size selection (col. 7, lines 28-40). The micelle or

inverse micelle technique is described to produce nanocrystals where "[v]ariations in size are generally in the range of $\pm 7\%$ in diameter" (col. 7, lines 10-11). Accordingly, although not noted by the examiner or appellants, it appears that Jaskie discloses a method of producing particles having a highly uniform distribution of diameters within the claimed range (although Jaskie does not specifically mention a 95 percent figure). Nevertheless, we also consider the examiner's reasoning.

The examiner finds that Jaskie does not disclose the claimed range of particle sizes (FR3). The examiner states (FR3): "Jaskie teaches, however, that the specification of a desired particle range is within the level of skill of the art. See col. 7, lines 34-40. It would have been obvious to specify a desired particle range because the specification of a desired particle range is generally recognized to be within the skill of the art." Appellants admit that "the Jaskie patent discloses ... the desirability of having highly uniform fluorescent particles" (Br5) and do not appear to challenge the examiner's conclusion.

The examiner further reasons that taking particles in Jaskie having a yellow color with a 50 Å (5 nm) size as the average particle size, the narrower $\pm 40\%$ range of particle size recited in claim 5 would require a range of particle sizes from 3 to 7 nm (FR3). The examiner reasons that the wavelength range of visible light from 400 to 800 nm would yield a particle distribution of

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from 4.14 to 5.84 nm which is within this range (FR3). That is, yellow light has a wavelength of about 590 nm which corresponds to a 5 nm particle size. Assuming the particle size is proportional to the wavelength, then blue light (at one end of the visible light range) with a wavelength of 400 nm has a particle size of 3.39 nm and red light (at the other end of the visible light range) with a wavelength of 700 nm (note that Jaskie discloses a range of 400 nm to 690 nm for visible light, col. 1, line 49) has a particle size of 5.93 nm, which is within the claimed range of particle sizes. Appellants do not challenge this reasoning. We agree that one of ordinary of ordinary skill in the art would have been motivated from Jaskie to select a highly uniform distribution of particles sizes in order to maintain a desired color. If one skilled in the art wanted to maintain a yellow color, for example, the range of particle sizes would be narrower than for the range of visible colors in the examiner's example.

The issue

Appellants do not contest that Jaskie discloses or makes obvious the particle size and uniformity limitations of claim 1. And, appellants do not contest that Jaskie discloses how to make particles having the claimed sizes mixed with other sizes. Instead, appellants argue that Jaskie does not enable one skilled

in the art to separate out particles into a batch having the claimed distribution range of sizes. Therefore, it is apparently appellants' position (although not expressly stated) that they are entitled to broadly claim the particle size and uniformity limitations without reciting the method of production because they were the first ones to come up with a method that allows production of particles having the claimed distribution of sizes.

The issue is whether Jaskie contains an enabling disclosure for making particles having the claimed distribution range of sizes. We agree that the disclosure must be adequate to permit one of ordinary skill in the art to make particles of the claimed size and size distribution. See Motorola Inc. v. Interdigital Technology Corp., 121 F.3d 1461, 1471, 43 USPQ2d 1481, 1489 (Fed. Cir. 1997) ("In order to render a claimed apparatus or method obvious, the prior art must enable one skilled in the art to make and use the apparatus or method.").

Jaskie is presumed enabled

Jaskie claims "particles each quantum confined by a diameter dictated by a specific desired color of emitted light" (claim 1) and having a diameter "less than approximately 100 Å" (claim 9). Jaskie discloses that a specific desired color, say yellow, corresponds to a particle diameter of about 50 Å (5 nm). For the particles to have a diameter dictated by the specific color

yellow, the diameters must be within a fairly narrow range around this diameter, much narrower than the range claimed by appellants, or other colors will be produced. Thus, the claims require particles of the claimed size and size distribution. Since Jaskie is a patent, it must be presumed that the disclosure enables one skilled in the art to make these particles. The presumption of validity puts the burden on appellants to prove that Jaskie does not have an enabling disclosure, rather than on the Office to prove that it does. The presumption may be overcome by sufficient evidence.

Jaskie teaches a method of preparing particles with uniform size

Jaskie discloses (col. 6, line 62 to col. 7, line 1):

There are presently a wide variety of methods for manufacturing quantum contained particles, at least one of which uses a Micelle technique that basically allows the particles to be made in a bucket using wet chemistry. The Micelle technique is a method of precipitation in a fluid in the presence of a stabilizer that binds to the growing crystal, preventing further growth or agglomeration.

Jaskie describes an inverse micelle² example for making nanocrystals (col. 7, lines 1-9) and states that "[v]ariations in size are generally in the range of $\pm 7\%$ in diameter" (col. 7, lines 10-11), implying that most particles are within this range, which is well within the claimed range. Thus, this technique of

² A description of "micelle" from the McGraw-Hill Encyclopedia of Science & Technology, Vol. 11 (7th ed. McGrawHill, Inc. 1992), pp. 117-118, is attached.

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making nanoparticles does not appear to require size selection. Jaskie refers to a symposium paper, "Observations of Melting in 30 Å Diameter CdS Nanocrystals" by A.N. Goldstein, V.L. Colvin, and A.P. Alivasatos, in "Clusters and Cluster Assembled Materials," Materials Research Society Symposium Proceedings, Fall 1990, at col. 7, lines 11-17, which we consider to be incorporated by reference. A copy of this paper is attached. The paper states (p. 271-72): "New developments in chemical methods of preparation, have enabled the synthesis of narrow size distributions of highly crystalline, nanometer size, crystallites of inorganic semiconductors like CdS and GaAs" (emphasis added). One footnote to this sentence refers to an article entitled "Surface Derivatization and Isolation of Semiconductor Cluster Molecules," by M.L. Steigerwald et al., J. Am. Chem. Soc. 110, 1988, pp. 3046-3050 (copy attached), which describes preparing molecules of semiconductor solid that are size-selected, in particular, clusters that "have a mean cross sectional dimension of 17(3) by 19(5) Å (where the numbers in parentheses are one standard deviation)" (p. 3048). Since one standard deviation includes about 68% of the things being measured and two standard deviations includes about 95% of the things being measured, it can be seen that two standard deviations is 17±6 by 19±10 Å which is within the claimed distribution. Although the Goldstein and Steigerwald references are not applied in the rejection, they are

indirectly relied on by Jaskie and clearly demonstrate that it was known to those in the art how to prepare nanoparticles with uniform size distributions.³ We find that Jaskie describes making nanocrystals by an inverse micelle technique with a $\pm 7\%$ range of variation of diameter. Appellants do not address this disclosed method of making nanocrystals of a uniform size either in the arguments or the expert declarations.

Jaskie also describes manufacturing quantum contained structures down to 10 Å by common etching techniques (col. 7, lines 17-27). It appears that these structures could be considered particles; claim 1 does not require the particles to be in a free or powder form.⁴ However, this method does not describe a range of particle sizes. Appellants do not address this method of making quantum contained structures.

³ This technique of isolating clusters of nanoparticles [nanoclusters) of specific sizes by terminating the particle surfaces is also evidenced by the discussion of nanoclusters in Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 18 (4th ed. John Wiley & Sons 1996), pp. 842-843, 859 (copy attached) at p. 843: "With the proper surface-capping agents, clusters of varying sizes can be isolated as powders" Kirk-Othmer is a standard reference work that is cited only to substantiate facts in the evidentiary showing.

⁴ This manufacturing technique also appears to be mentioned in Kirk-Othmer, p. 843: "[S]emiconductor nanoclusters can be directly synthesized in the polymer film (26-30).".

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Appellants' arguments and expert declarations are not persuasive to show that Jaskie lacks an enabling disclosure

Jaskie discloses (col. 7, lines 28-40):

The tuning (size selection) is also accomplished in a variety of ways, at least one of which includes a wet filtering technique. The quantum contained particles (of all sizes) are suspended in a wet mixture. One end of a cloth is immersed in the liquid and the mixture is allowed to move up the cloth by capillary action, aided by an electric field if desired. The quantum contained particles will move up the cloth a distance directly proportional to their size. Thus, at a predetermined height on the cloth all of the quantum contained particles will be substantially the same size. Utilizing this or a similar technique the quantum contained particles can be easily separated into desired sizes.

This describes a method of separating quantum contained particles based on their size.

Appellants argue that "the production of particles with the claimed narrow particle size distribution was not within the level of skill in the art" (Br6) and "the discussion in the Jaskie patent [of wet filtration at col. 7, lines 28-40] did not permit the formation of the narrow particle size distributions disclosed and claimed by Applicants" (Br6) as evidenced by the declarations of Professor Singh and Professor Bricker (Br6). That is, it is argued that the wet filtration method of Jaskie does not enable one of ordinary skill in the art to make the claimed invention. Appellants' arguments are best addressed in connection with the declarations on which they are based.

Singh declaration

Professor Singh is a consultant to the assignee NanoGram Corporation (Singh decl. ¶ 5) and therefore is not a totally disinterested party. Nevertheless, Prof. Singh has impressive credentials and his testimony must be given weight.

Initially, we note that Prof. Singh's declaration does not address making of uniform sized particles by the disclosed inverse micelle technique in Jaskie, which is said to produce particles having a variation in size of $\pm 7\%$ (col. 6, line 62 to col. 7, line 17). Nor has Prof. Singh discussed Jaskie's description of making quantum confined structures by etching (at col. 7, lines 17-27), where the particles are on a surface instead of in a free form. Prof. Singh's education and experience do not appear to be in the area of preparing nanoparticles by the chemical inverse micelle technique or the etching technique. Thus, even if Prof. Singh's declaration is persuasive as to nonenablement of Jaskie's wet filtration process, the declaration fails to show that other methods in Jaskie do not enable one of ordinary skill to make the claimed invention. Although the declaration is not persuasive for this reason, we nevertheless also consider Prof. Singh's testimony regarding the wet filtration method.

Prof. Singh states that, to his knowledge, no experimental results based on the separation of nanoparticles by the wet

filtration process described by Jaskie have ever been reported in the literature (Singh decl. ¶ 7) and since such chromatography techniques are not known for the separation of nanoparticles, a person of ordinary skill in the art would be expected to expend a substantial amount of inventive effort to practice the wet filtration technique and, absent at least some preliminary results, there would be no reasonable expectation of success (Singh decl. ¶ 7). Prof. Singh offers his opinion that the wet filtration approaches in Jaskie are highly speculative (Singh decl. ¶ 7). Prof. Singh states that based on his extensive knowledge in the nanoparticle field, it is his opinion that tuning could not be performed by the wet filtration approach outlined in Jaskie without the expenditure of an undue amount of experimentation (Singh decl. ¶ 10).

The examiner states that Prof. Singh "fails to disclose what data basis [sic, databases], public records, or patent files" (EA6) were searched, or "what search terms, logical statements, or search strategy" (EA6) were applied to support his statement that wet filtration is not described in the literature (EA6).

Appellants responds that "Professor Singh is one of the best experts in the world to attest to such a fact, i.e., that the Jaskie separation approach is not known to persons of skill in the art" (RBr5-6) and "Professor Singh is an invited speaker at most of the major particle science conferences in the world and

is, thus, aware of the cutting edge research being performed in the world" (RBr6).

While Prof. Singh's has impressive credentials, a person cannot be expected to know everything in the art. This is the reason for the hypothetical person of ordinary skill standard in obviousness. We think it is not unreasonable, in questioning the enablement of a patent, to require some searching of the literature rather than reliance on personal knowledge to support a statement that Jaskie's method was not described in the literature. The burden of showing lack of enablement is on appellants. Prof. Singh's conclusion that it would require an undue amount of experimentation to make the wet filtration approach work is evidently based solely on his lack of personal knowledge of any description of the process in the literature. However, since we have no evidence of a search we can give little weight to Prof. Singh's statement that the process is not described in the literature or the conclusion that undue experimentation would be required. Prof. Singh's statement that the filtration approach in Jaskie is highly speculative is a mere conclusion which is not supported by any factual reasoning as to why the process would be unlikely to work as described. Thus, these statements by Prof. Singh are not entitled to weight.

The examiner states that the declaration does not present any experimental results, evidence of tests conducted, methods

evaluated, or any factual evidence, but consists of mere arguments and conclusions (EA5-6).

Appellants argue that no experiments are performed without relying on the experience of the experimenters, experiments must be designed and interpreted, and "Professor Singh's Declaration is ... based on a multitude of experiments performed by himself and his students [over the years]" (RBr4).

Nevertheless, past experiments which form the basis for Prof. Singh's experience and expertise are not experiments which show whether the wet filtration in Jaskie will work. In any case, the declaration does not provide any factual reasons, based on such prior experiments, why the wet filtration method in Jaskie would not be expected to work.

Prof. Singh states that since the Jaskie wet filtration technique would be difficult or impossible to scale up to commercial quantities, it is unlikely that any effort will ever be spent on developing such approaches (Singh decl. ¶ 8).

Whether or not effort would be spent developing the Jaskie process does not tend to show that the Jaskie technique is unworkable as described to one of ordinary skill in the art.

Prof. Singh states that at the time of filing there were no filtration approaches publicly known that could create a collection of phosphorescent nanoparticles with a very narrow

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size distribution and, at best, these filtration techniques could only exclude micron scale contaminants (Singh decl. ¶ 9).

This statement can be considered to be related to the statement in Jaskie that "[t]he tuning (size selection) is also accomplished in a variety of ways" (col. 7, lines 28-29) and the question of whether one of ordinary skill in the art knew of other ways to perform size selection. Assuming it is correct that there were not other publicly known filtration approaches for nanoparticles, this does not prove that the wet filtration approach will not work and does not prove that other approaches for size selection were not known.

For the reasons stated above, the declaration of Prof. Singh is not entitled to weight.

Bricker declaration

The declaration by Professor Bricker, submitted with the amendment after final on October 10, 2000 (Paper No. 21), was deemed untimely by the examiner and it was noted that it would not be considered in the advisory action of October 20, 2000 (Paper No. 22). Nevertheless, since the examiner's answer refers to the declaration by Prof. Bricker, it appears to have been considered and will be addressed here.

Initially, we note that Prof. Bricker's declaration also does not address making of uniform sized particles by the

disclosed inverse micelle technique in Jaskie, which is said to produce particles having a variation in size of $\pm 7\%$ (col. 6, line 62 to col. 7, line 17). Nor does Prof. Bricker discuss Jaskie's description of making quantum confined structures by etching (at col. 7, lines 17-27). Prof. Bricker's education and experience do not appear to be in the area of preparing nanoparticles by the chemical inverse micelle technique or the etching technique. Thus, even if Prof. Bricker's declaration was persuasive as to nonenablement of Jaskie's wet filtration process, the declaration fails to show that other methods in Jaskie do not enable one of ordinary skill to make the claimed invention. Although the declaration is not persuasive for this reason, we nevertheless also consider Prof. Bricker's testimony regarding the wet filtration method.

Prof. Bricker's declaration of unworkability seems to be based on the fundamental assumption that a process where a mixture of different sized particles is continuously loaded onto the cloth will not work to separate different size classes of quantum particles because particles are continuously remixed with particles of other sizes as additional particles are loaded onto the cloth (Bricker decl. ¶ 9). We interpret this to mean that if it is assumed that 50 Å particles climb to 10 inches and 30 Å particles climb to 11 inches, under Jaskie's technique one can never separate out 50 Å particles because there is always some

smaller particles on their way through this zone on the way to a higher point in a continuous process.

The flaw in this reasoning is that Jaskie does not say that the process must be continuous (or commercial). The process can be a one-time run where the particles climb to a level depending on their size and the cloth is cut at an appropriate zone to retrieve particles of a specific desired size range. Because the declaration seems to be based on an erroneous assumption, Prof. Bricker's declaration is not persuasive.

Prof. Bricker also discusses that Jaskie provides no direct information on the properties of the liquid that the particles are suspended in, the surface characteristics of the cloth, or the surface properties of the quantum particles (Bricker decl. ¶ 10). It is stated that "the surface properties of the cloth used in the described separation is critical" (Bricker decl. ¶ 10) and that no cloth exists which provides differential partitioning of the solutes, i.e., the quantum particles, between a mobile phase and a stationary phase, the cloth (Bricker decl. ¶ 10). It is argued that the addition of an electric field would not solve these problems (Bricker decl. ¶ 11).

To the extent these reasons are dependent on the assumption of a continuous process, the reasons are not persuasive as already discussed. In addition, we note that the description in Jaskie is directed to the person of ordinary skill in the art,

which is the art of separating solid inorganic nanoparticles, and thus does not need to disclose details which would be known to the person of ordinary skill. Prof. Bricker's declaration is not persuasive because it relies on the lack of express teachings of materials in Jaskie without addressing what would have been known one of ordinary skill in the art.

Jaskie also discloses that "[t]he tuning (size selection) is also accomplished in a variety of ways" (col. 7, lines 28-29), although the only way described is wet filtering. Assuming that Prof. Bricker is correct that Jaskie does not enable one skilled in the art to make the claimed narrow particle size distributions by the wet filtration process, there is no evidence that one skilled in the art would not know of any other way to provide the required size selection.

For the reasons stated above, the declaration of Prof. Bricker is not entitled to weight.

Millipore product literature

Appellants cite product information in the brief from Millipore Corporation (Millipore) to show that commercial filters are not an effective means of creating narrow particle size distributions (Br15).

The examiner states that the fact that appellants have found a vendor that provides a filter that is not suitable for

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nanoparticle separation is not persuasive evidence that no such filter exists (EA7).

Appellants respond that the Millipore represents the latest advances in filtration technology for improving size uniformity and the fact that it is dated two years after appellants' filing date and does not disclose the filters has significant probative value (RBr6).

We agree with the examiner's position. The purpose of Millipore filters is to retain the small number of defect causing "large" particles (> 1 micron) without retaining the desirable, small particles (30 to 200 nm). This does not prove that filters to filter out particles outside of a certain range do not exist or cannot be built. Appellants' argument based on Millipore is not persuasive that Jaskie is not enabled.

Parker patent

In the examiner's answer, the examiner refers to U.S. patent 5,460,701 to Parker et al. as disclosing the use of a mechanical filter for the collection of nanocrystals (EA7). Parker is not applied in any ground of rejection.

Appellants argue that while Parker describes a filter for collecting nanoparticles, the collection process does not discriminate in size and is not relevant to the issue of size

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separation to produce a more uniform collection of particles (RBr7).

We agree with appellants' argument and find the examiner's reasoning to be unpersuasive.

Lithium separation

In the final rejection, the examiner referred to the use of chromatography to separate lithium-6 from lithium-7 (FR6).

Appellants argue that while chromatography is a well developed field for chemical and biochemical separation, this experience does not extend to the separation of solid inorganic particles by size (Br11). It is argued that the examiner's reference to isotope separation of lithium is nonpersuasive because there is no expectation that ion-exchange chromatography would be expected to work for inorganic nanoparticles to separate them by size (Br11-12).

The examiner does not rely on the lithium example in the examiner's answer. Nevertheless, we agree with appellants' argument and find the examiner's reasoning to be unpersuasive.

Conclusion

We find that Jaskie discloses a method of making nanoparticles having a variation in size of $\pm 7\%$. This teaching has not been addressed in appellants' arguments or in the

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OBSERVATION OF MELTING IN 30 Å DIAMETER CdS NANOCRYSTALS

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ABSTRACT

Temperature dependent electron diffraction studies on 30 Å diameter CdS nanocrystals are described. The linear thermal expansion coefficient of the nanocrystals is 2.75×10^{-4} Å/K, and the melting point is 575 K. These data are in contrast to bulk CdS which has a melting point of 1750 K and a linear expansion coefficient of 5.5×10^{-4} Å/K. The observed depression in the melting point of these semiconductor clusters is similar to effects observed in metals and molecular crystals, indicating that the phenomenon of reduced melting point in small systems is a general one regardless of the type of material. The observation of melting point depression in these clusters also has far reaching implications for the preparation of highly crystalline clusters of CdS, as well as for the use of these nanocrystals as precursors to thin films.

INTRODUCTION

The reduction of the melting point in nanometer size metal and molecular crystals is well established experimentally^{1,2}, and is the subject of numerous theoretical studies and simulations^{3,4}. It is of interest to extend these studies of melting to other classes of materials. In particular, systems in which the bonding is more covalent and the structure more open, may behave differently. Also, studies of covalent systems would extend current models of melting which rely on the concept of surface tension, a term difficult to define for a covalent cluster. Finally, the study of melting in any cluster material lends insight into the stability of these metastable systems, an issue vital to the development of new synthetic methods.

Despite the many reasons to study melting in clusters, the field has been until recently limited to metals and molecular crystals. New developments in chemical methods of preparation, have enabled the synthesis of narrow size distributions of highly crystalline,



Figure 1 TEM of a CdS Nanocrystal of the type studied in this paper. The $\langle 111 \rangle$ axis is parallel to the beam axis.

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nanometer size, crystallites of inorganic semiconductors like CdS and GaAs²¹. These materials are polar semiconductors and have open structures. They are large enough to possess the bulk zincblende crystal structure, but a large fraction of the atoms are on the surface. Hence, as in the metal clusters, it is expected that the surface will play a dominant role in their high temperature behavior. Unlike metal clusters, these semiconductor nanocrystals must have ligand stabilizers on the surface in order to prevent aggregation of the colloids. It is expected that these organic terminating moieties on the surface will also influence the melting of these nanocrystals.

EXPERIMENTAL

30 Å diameter CdS nanocrystals were prepared using the reverse micelle method⁴. Two separate solutions of 500 ml spectrographic grade heptane and 44.4 g of dioctyl sulfosuccinate (A.O.T.) were prepared under nitrogen. 2.34 g of CdCl₂ • 6H₂O dissolved in 12 ml deoxygenated deionized water were added to one solution while 0.36 g Na₂S • 9H₂O dissolved in 12 ml deoxygenated deionized water were added to the other. Both solutions were clear and colorless after one hour of mixing. The cadmium solution was transferred to the well stirred sulfide solution via a 16 gauge double transfer needle over 15 minutes, resulting in the formation of a clear yellow solution of CdS nanocrystals. 500 ml of the resulting solution was "capped" with 0.45 mg of thiophenol, which resulted in precipitation of the nanocrystals. The powder was filtered and rinsed repeatedly with petroleum ether. The powder was redissolved in 10 ml pyridine, filtered, reprecipitated by addition to 200 ml petroleum ether, filtered and rinsed again. The powder was redissolved in quinoline, and refluxed under inert atmosphere at 237 °C for 3 hours. Finally, the nanocrystals were reprecipitated and filtered one more time. The resulting powder was dissolved in pyridine and deposited by evaporation on an amorphous carbon substrate evaporated onto a 300 mesh Ni grid for the electron diffraction studies.

Heating studies are conducted on a 0.2 μm² field of particles in a JEOL 200 CX AEM (200 kV) electron microscope at the National Center for Electron Microscopy at the Lawrence Berkeley Laboratory. The condenser and objective lens currents were controlled to ±0.002 amps with an electron flux of about 800 e-/Å² sec in the specimen plane, well below the fluxes commonly required to cause beam-induced transformations (more than 10,000). Calculations of beam induced

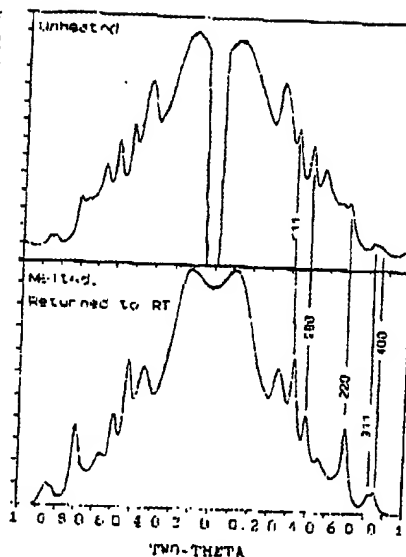


Figure 2 Electron Diffraction from 30 Å diameter CdS nanocrystals before and after melting.

heating indicate less than 6 K temperature rise induced by the electron beam. The specimen temperature was controlled using a tantalum hot stage. The beam flux and the exposure time were maintained constant, and the electron diffraction patterns were collected at a series of temperatures. The samples were examined by energy dispersive spectroscopy before and after the heating experiment in order to monitor possible changes in the elemental composition (none were found). Real space images before and after heating are used to determine morphological changes in the nanocrystals.

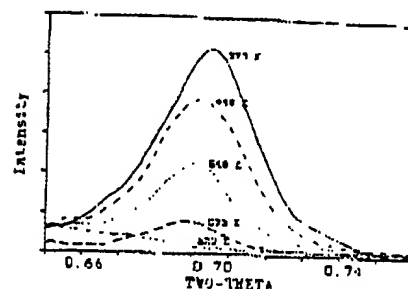


Figure 3 The 220 diffraction peak at several temperatures.

RESULTS

The temperature dependence of the electron diffraction pattern from 30 Å diameter CdS nanocrystals is illustrated in Figures 2, 3, and 4. In the room temperature pattern of Figure 2, the 111, 200, 220, 311, and 400 peaks of zincblende CdS can be seen superimposed on the background from the transmitted electron beam. Three additional peaks, due to the amorphous carbon substrate, can be seen as well. As the sample is heated the intensity of the electron diffraction peaks of the CdS drops off. This is illustrated for the 220 peak in Fig. 3. Figure 4 shows the logarithm of the intensity of the 111, 200 and 220 peaks versus temperature. Between 550 and 580 K the intensity of these peaks abruptly decreases more than two orders of magnitude. When the sample is returned to room temperature, the original CdS nanocrystal electron diffraction pattern is recovered (Figure 2, lower panel). The intensity of the diffraction from the recrystallized particles is higher, and the width of the peaks is about 5-10% narrower due to an improvement in the crystallinity within the particles. At high coverages fusion of the nanocrystals occurs, resulting in the formation of a sintered, polycrystalline film whose domain size is comparable to the size of nanocrystals initially deposited.

Discussion

The abrupt disappearance of the electron diffraction pattern of CdS nanocrystals at 575 K is due to melting of the 30 Å diameter clusters. This is the first demonstration of the melting point reduction in a semiconductor nanocrystal, and is in agreement with studies of metal clusters which also

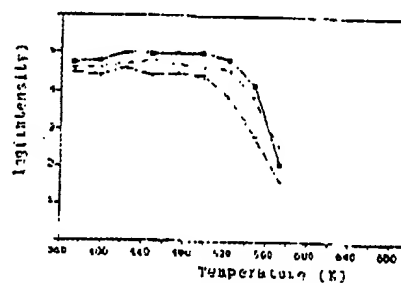


Figure 4 Log Intensity vs. T for 3 peaks in the diffraction pattern. The sharp drop at 575K is due to melting.

exhibit a depressed melting point. This result helps to clarify the role of refluxing in cluster synthesis. It has been observed that refluxing of clusters in high boiling solvents improves cluster crystallinity, which in light of the melting point reduction makes sense. A more detailed study of thermal properties of these systems is in progress.

ACKNOWLEDGMENTS

We wish to thank C. Echer for his help in acquiring analytical and diffraction data, as well as M.A. O'Keefe and J.H. Turner for their assistance in digitizing the diffraction data. We acknowledge the National Center for Electron Microscopy at the Lawrence Berkeley Laboratory for the use of their facilities.

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$\times 10^{-14}$ J. If this energy is converted completely into visible photons (energy $\sim 4 \times 10^{-19}$ J), the total number of photons is $7 \times 10^{-14} / 4 \times 10^{-19} \sim 2 \times 10^5$. Taking account of the light collection efficiency (~ 0.004), the number of photons collected per diode array channel is ~ 0.8 , which could hardly be detected. Considering also the efficiency of energy conversion from discharge to emission, the energy consumed for the excitation of TSE should be several orders of magnitude higher than E estimated above. Namely, most of the electrical energy must be used in the internal discharge across the microcracks.

The rise and decay times and pulse width of V_{TSE} exhibit a pulse-to-pulse variation in synchronism with V_{Py} . The fastest decay time of TSE (~ 20 ns) is shorter than the normal decay time (~ 0.7 ns) for PL.¹⁴ These facts indicate that the excited state involved in TSE must have a much faster decay rate than that in PL. Generally the PL emission from UO_2^{2+} shows no dependence on the excitation wavelength;¹⁵ i.e., there is no possibility of emission from vibrationally excited $^3\Pi_1$ state. Therefore the shorter lifetime of TSE cannot be explained on this basis. The most plausible explanation for this would be that the UO_2^{2+} ions near the crack surface are involved in TSE where the environment of the ions is different from that in the bulk and results in a faster nonradiative decay from the vibrationless $^3\Pi_1$ state. The blue shift

of the TSE spectrum with respect to the PL spectrum should also be due to the unusual environment near the crack surfaces.

C. Summary. We have shown that TSE observed for a single crystal of UNH has the same spectroscopic origin as photoluminescence ($^3\Pi_1 \rightarrow ^1\Sigma_g^+$ transition in UO_2^{2+}) with a remarkable blue shift. Simultaneous time-resolved measurements of the TSE and PyE pulses have established the correlation between the luminescence and the electric charge separation. The piezoelectricity coupled with microcrack formation has been revealed to be the main cause for the temperature-induced charge separation. It has also been suggested that the charge neutralization across the microcrack is most probably responsible for the TSE excitation. This mechanism is essentially the same as that proposed so far for TL, except that the stress is not caused by an external force but caused internally by temperature change. We hope that the present investigation would reveal not only the mechanism of TSE and charge separation accompanied but also some further details of the TL phenomenon. We have also suggested the possibility of phase transition involved in the process. Further investigation on the crystal structure and thermal measurements would clarify this point.

Acknowledgment. One of the authors (H.D.B.) is indebted to Prof. S. Nagamura, Director General, IMS for providing a visiting assignment at IMS, to Prof. D. D. Pant and D. P. Khazdewal for the gift of the UNH sample, and to Prof. H. Inokuchi and Dr. T. Enoki for help during the experimental work.

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Surface Derivatization and Isolation of Semiconductor Cluster Molecules

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Abstract: We describe a synthesis of nanometer-sized clusters of CdSe using organometallic reagents in inverse micellar solution and chemical modification of the surface of these cluster compounds. In particular we show how the clusters grow in the presence of added reagents and how the surface may be terminated and passivated by the addition of organoselenides. Passivation of the surface allows for the removal of the cluster molecules from the reaction medium and the isolation of organometallic molecules which are zinc blende CdSe clusters terminated by covalently attached organic ligands. Preliminary cluster characterization via resonance Raman, infrared, and NMR spectroscopy, X-ray diffraction, transmission electron microscopy, and size-exclusion chromatography is reported.

Large inorganic cluster molecules are interesting as representatives of a state of matter intermediate between molecules and crystalline solids.¹ The differences are especially evident in molecules that are fragments of the lattice of infinite solid-state compounds.² Recent studies of bare semiconductor crystallites (stabilized as colloids) have described electronic properties that depend on the size of the colloidal particles³ and have thereby

yielded insight into the transition from the molecular regime to the solid state. It is important for further examination of this transition to be able to prepare and isolate true molecules of the semiconductor solid that are size-selected, having from 100 to 10⁴ atoms, are soluble in convenient solvents, and are chemically protected from growth and aggregation into bulk solids.

Colloids of II-VI crystallites small enough (≤ 50 Å) to have incomplete band structure were first prepared by arrested precipitation in homogeneous solution.³ Better size control and dispersion stability were achieved by arrested precipitation in structured media (zeolites, inverse micelles, polymer films, etc.).⁶

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Mezzanin and collaborators first isolated re-dispersible powders of colloidal clusters protected by polymeric cadmium hexamethylenephosphates.⁴ This paper reports synthesis and isolation of a family of molecular CdSe fragments. Arrested precipitation in reverse micelles gives a bare semiconductor lattice, and in situ molecular modification of the cluster surface enables isolation of the molecular product with a variety of organic surface ligands.

Experimental Section

General. All manipulations involving alkylcadmium reagents were carried out with standard airless techniques. The carboxenat bis(2-ethylhexyl) sulfosuccinate (Aeracel-OT; AOT) was used as purchased from Aldrich, as was LiHBEt. Metal salts were used as purchased from Alfa. Standard solutions of Cd²⁺ (1.0 M) were prepared from Cd(ClO₄)₂·6H₂O and deaerated water. Hexanes, thf, and pyridine were anhydrous, purchased from Aldrich, and petroleum ether was 35–60 °C, purchased from Mallinckrodt. Water was routinely deaerated by ebullition with nitrogen. The alkylcadmium and alkyltellurium reagents were prepared via literature methods⁵ and stored at 0 °C in the dry state. Throughout the text Se(TMS)₂ stands for bis(trimethylsilyl)tellurium, PhSeTMS for phenyl(trimethylsilyl)tellurium, and Te(TBDMS)₂ for bis(*tert*-butyldimethylsilyl)tellurium. The ratio *W* is defined as the molar ratio [H₂O]/[AOT]. Values of *W* are nominal, given by the ratio of water purposely added to initial conc. Corrections to account for hygroscopicity and/or water of hydration of the soap were not made and were found to be not important in this work.

Preparation of a Typical AOT/H₂O/Heptane Microemulsion. The surfactant AOT (33.3 g, 75 mmol) is purified and degassed by dissolving the solid in petroleum ether, filtering to remove particles, and evaporating the filtrate to dryness. The dried surfactant is redissolved in heptane (1300 mL), and deaerated water (4.3 mL) is added. The mixture is stirred magnetically until the mixture becomes homogeneous. This preparation gives a microemulsion with *W* = 3.2.

Typical Preparation of Surface-Modified CdSe Particles. An aliquot (1.12 mL) of the standard Cd²⁺ solution is added to the above microemulsion. Stirring gives an optically homogeneous microemulsion with *W* = 4.0. A solution of Se(TMS)₂ (210 µL, 0.93 µmol) in heptane (50 mL) is added quickly to the microemulsion via syringe. A color develops throughout the homogeneous microemulsion as the semiconductor particles form. The absorption spectrum of the solution shifts to its final, persistent form over the time of seconds (for large *W*) to minutes (for small *W*). This surfactant-stabilized colloid can be treated in a number of ways subsequent to this preparation: (1) further surface chemical modification (see below); (2) evaporation to dryness; or (3) flocculation. Evaporation of the microemulsion to dryness yields colored solid surfactant in which the CdSe particles are embedded. This surfactant-particle composite may be redissolved in hydrocarbon to give an optically homogeneous solution. These solutions are stable indefinitely, showing little or no sensitivity to air and/or room light, although some deterioration has been noticed over the space of 8–10 months in solution samples that have been left unprotected from air and light.

If the CdSe-containing microemulsions are not evaporated to dryness (thereby removing the sequestered water), flocculation of the semiconductor particles occurs within hours. Flocculation occurs immediately if a large amount of water is added directly to the as-prepared microemulsion. The flocculated solid does not redissolve in any common organic or inorganic solvent.

Typical Preparation of "Fragile-Capped" CdSe Molecular Particles. A sample of surfactant-stabilized CdSe particles is prepared as above. The surface of the particles is coated with Cd²⁺ by the addition of 0.5 mL of the stock Cd(ClO₄)₂ solution. After the emulsion becomes optically homogeneous once more, PhSeTMS (350 µL, 1.5 mmol) in 50 mL of heptane is added via syringe. The mixture becomes cloudy, and a colored precipitate is collected either by centrifugation or filtration. Exhaustive washing with petroleum ether followed by air-drying gives a free-flowing powder.

The yield from the above sequence is 260 mg. This is 53% of the total combined mass of Cd, Se, and Ph added to the reaction mixture. The capping reagent (PhSeTMS) is added in excess, and any unused PhSeTMS and any possible byproducts such as Ph₂Se₂ are removed during the purification process. Similarly, a deficiency of Se(TMS)₂ is used in the first step. Therefore, in a sense, Cd²⁺ is also in excess at points along the preparation. These two points make the interpretation of the percent yield a bit vague. If it is assumed, based on overall

stoichiometry, that Cd is the limiting reagent, the yield from the above reaction is 67%. The average yield from our preparations (0 < *W* < 10, absolute mass of reagents within an order of magnitudes of those cited above) has been ~35% based on total input mass, or ~75% based on Cd as the limiting reagent.

Samples prepared according to the given prescriptions dissolve completely in pyridine. Addition of petroleum ether causes reprecipitation of the semiconductor material. This sequence can be used to remove any truly flocculated colloid material from the molecular particles, since the flocculated material does not dissolve in pyridine. Precipitation of insoluble, flocculated material has been indicative of incomplete surface passivation and can generally be avoided.

Preparation of Powders of II–VI Materials with Silylalkylcadmium Reagents. We have prepared CdSe, HgSe, and CdTe using Se(TMS)₂ and Te(TBDMS)₂, and the corresponding metal salts (Cd(ClO₄)₂ or HgCl₂). The procedure is the same for all three cases; we describe the preparation of HgSe.

A solution of Se(TMS)₂ in thf (ca. 0.3 M) is prepared, starting with 0.53 g (6.7 µg-atom) of cadmium powder, 13 mL (15 mmol) of LiHBEt, in thf, and 1.45 g (15 mmol) of (CH₃)₃SiCl. Subsequent to formation, this material is transferred via cannula to HgCl₂ (1.02 g, 15 mmol) in 10 mL of thf. Immediately on addition a jet-black precipitate forms. After complete addition the mixture is filtered (in air) to give a black solid that is washed (H₂O, acetone, then Et₂O) and dried in air to give 1.67 g of black solid whose X-ray powder pattern shows only HgSe. This gives 92% yield of HgSe, based on HgCl₂.

The preparations of CdSe and CdTe are identical except that the X-ray powder patterns of the precipitated powders showed no peaks (neither starting materials, products, nor byproducts), using our routine instrument. Annealing the powders (temperatures from 250 to 500 °C) gave powders whose patterns showed only CdSe and CdTe, respectively. We rationalize this based on the lower diffusivity of Cd, which requires higher temperatures for crystallization of the Cd materials than the corresponding Hg compounds.

At no point during any of the preparations of bulk HgSe, CdSe, or CdTe was there any evidence for the formation of any other phase. Specifically, no elemental chalcogen was ever observed.

Results and Discussion

Arrested precipitation from inorganic aqueous ions has proven to be quite useful in preparing semiconductor colloids. We became interested in extending this methodology and were led to bis(trimethylsilyl)chalcogenides by several reports in the literature which describe these compounds as organometallic equivalents of chalcogenide dianions.^{1(a,c)}

We initially observed that treatment of Cd(ClO₄)₂·6H₂O with an equimolar amount of Se(TMS)₂ in THF at room temperature gave immediate precipitation of a red-brown solid whose X-ray powder pattern showed no reflections. Subsequent annealing of this solid gave hexagonal CdSe as the only observed solid-state compound. This preparative scheme was extended to HgSe (by using HgCl₂ in place of Cd(ClO₄)₂·6H₂O) and to CdTe (by using Te(Si(CH₃)₂(C(CH₃)₂)₂)₂ in place of Se(TMS)₂). In each case the II–VI compound of interest is the only solid-state product observed in the X-ray analysis.

Given these results, we then attempted to control the crystallite growth by performing the reaction in AOT/H₂O/heptane reversed micelle solutions. Several groups have shown that the ratio *W* = [H₂O]/[AOT] controls the size of colloidal crystallites formed from ionic reagents.^{6(a–c)} We observe that the organometallic reactions described above readily occur in reverse micelle solution. After Cd²⁺ was dissolved in the water pools of AOT/H₂O/heptane solutions (at a concentration of approximately one ion per pool) the resulting solution was treated with a heptane solution of Se(TMS)₂. This immediately produces intense color. A UV-vis spectrum characteristic of CdSe cluster crystallites⁷ is observed. The crystallite absorption threshold shifts red with increasing *W*, as expected for increasing crystallite size (Figure 1). Transmission electron microscopy directly images CdSe crystallites in thin AOT soap films made by colloid evaporation (Figure 2). These internal

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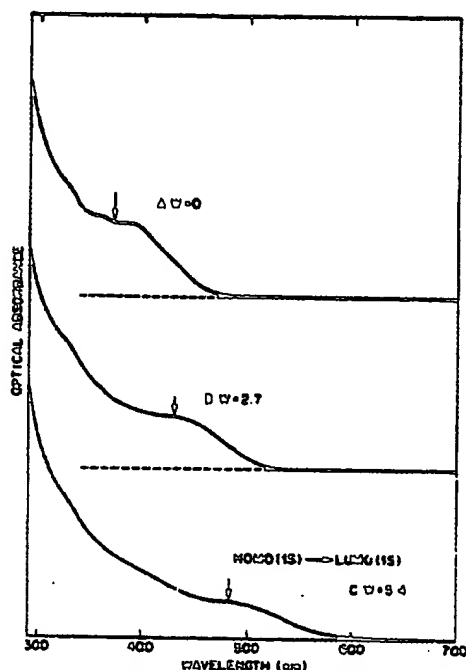


Figure 1. Optical absorption spectra (25 °C) of CdSe clusters synthesized and stabilized in microemulsion media. Synthesis conditions: [AOT] = 0.05 M, $[Cd(ClO_4)_2] = 7.5 \times 10^{-4}$ M, $[Se(TMS)_2] = 5 \times 10^{-4}$ M; (A) $W = 0$; (B) $W = 2.7$; (C) $W = 5.4$. The lowest, size dependent HOMO \rightarrow LUMO transition is marked with an arrow in each case. The curves are offset vertically for clarity.

lattice images allow analysis of the size, shape, and internal unit cell of crystallites. Crystallites with (111) axes in the micrograph plane show alternating light and dark lines representing planes of atoms. The clusters show a narrow size distribution for smaller sizes made at low W . The clusters corresponding to Figure 1a ($W = 0$) have a mean cross sectional dimension of 17 (3) by 19 (5) Å (where the numbers in parentheses are one standard deviation). As the repeat distance along (111) is 3.51 Å, these particles vary in diameter by only one CdSe layer. Larger W preparations yield larger crystallites; a lowest discrete state at ~ 330 nm corresponds to ~ 45 Å diameter with a 25% standard deviation.

Thus this reaction yields micelle-encapsulated colloidal CdSe crystallites, in a fashion analogous to the previously reported syntheses of CdS in reverse micelles.²⁰ In order to understand the mechanism of size control in these preparations, we performed the growth experiment summarized in Figure 3. To 120 mL of heptane solution containing AOT (3.3 g; 0.05 M), water (420 μ L, 0.22 M), and Cd^{2+} (as the perchlorate, 0.06 mmol; 5×10^{-4} M) was added $Se(TMS)_2$ (0.044 mmol in 7 mmol of heptane). This gave small crystallites of CdSe as shown by UV-vis spectroscopy (trace a in Figure 3). Subsequent to this seed formation, alternate aliquots of Cd^{2+} and $Se(TMS)_2$ were added. After each addition the UV-vis spectrum was recorded (traces b and c in the figure). These data show no change on addition of excess Cd^{2+} (since the system is already Cd-rich) and a shift of the onset of absorption to longer wavelength upon addition of $Se(TMS)_2$. The shift shows that rather than forming more particles of the same size as the original ones, the new cadmium and selenium reagents add to the original CdSe crystallites, giving larger particles. In this sense the colloidal crystallites are inorganic living polymers: the crystallites are stable in the reverse micelles, yet their surfaces are reactive. Although this experiment is not conclusive, it does suggest a growth mechanism for arrested precipitation in micelles. We propose that particle growth occurs by addition of atoms (or ions) one at a time, by exchange of Cd^{2+} between water pools, and by an organometallic reaction at the interface. The micelle prevents contact between two large (growing) crystallites, and the

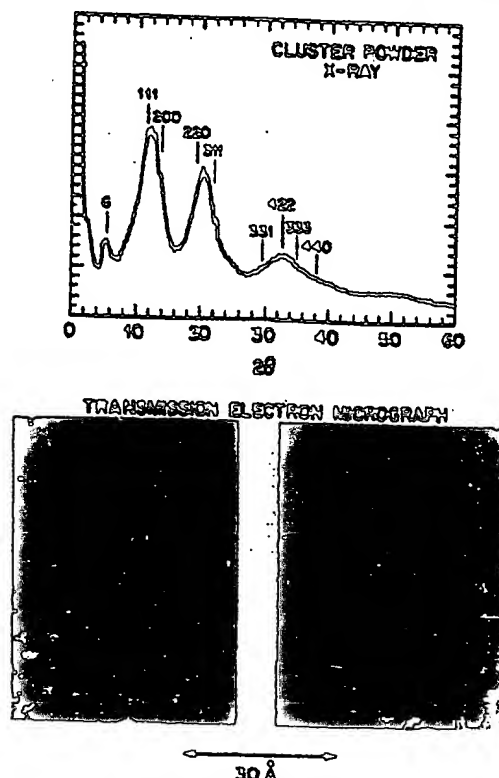


Figure 2. Top: X-ray powder pattern of phenyl-capped CdSe cluster powder. Positions of CdSe bulk zinc blende lines are marked. G stands for silicone grease used as a powder support. Bottom: Bright field transmission electron micrographs showing faint images of CdSe cluster internal lattice structure. A crystallite (111) axis lies in the plane of the supporting substrate producing the pattern of alternating light and dark lines. The amorphous carbon substrate produces an underlying speckle pattern. At this large magnification, the crystallite shape and edges become diffuse.

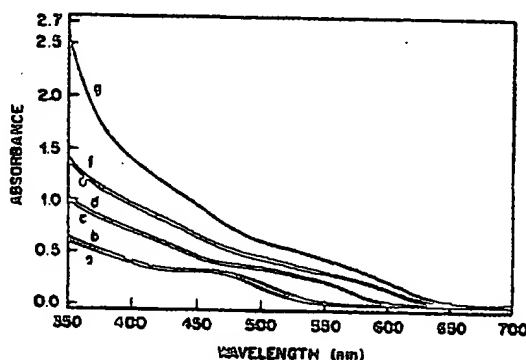


Figure 3. UV-visible spectra of the CdSe growth experiment. Traces a through f are in the heptane/AOT/ H_2O reaction medium, with the starting cadmium-containing solution as the reference. Trace g is in pyridine with pure pyridine as reference. After addition of (a) 44 μ mol of $Se(TMS)_2$ to the initial Cd^{2+} solution (see text); (b) 30 μ mol of Cd^{2+} (as a micellar solution); (c) 20 μ mol of $Se(TMS)_2$; (d) 30 μ mol of Cd^{2+} ; (e) 30 μ mol of $Se(TMS)_2$; (f) 60 μ mol of Cd^{2+} . (g) Spectrum of capped CdSe molecular particles after isolation, washing, and redissolution in pyridine.

crystallites grow until the supply of feedstock Cd and Se is exhausted. In this way size control is statistical (only a very small fraction of the micelles are eventual hosts to a CdSe particle) and kinetic (once a growth atom (ion) is attached to a growing

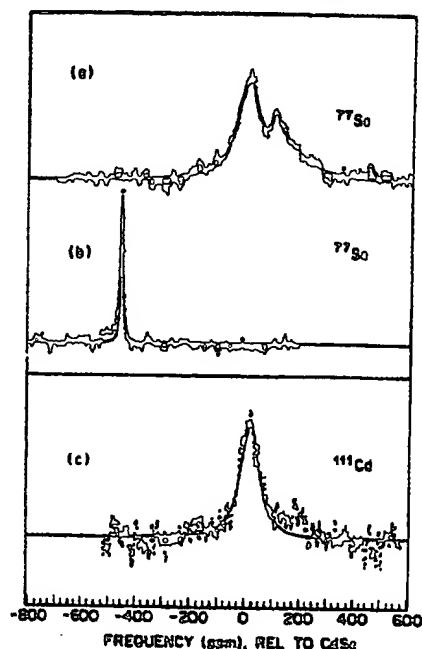
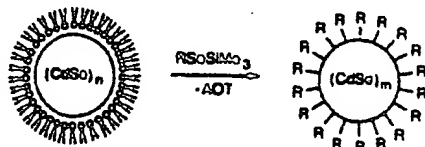


Figure 4. ^{77}Se and ^{111}Cd NMR spectra of capped semiconductor clusters dissolved in pyridine. Spectra are plotted on the σ scale (negative shifts corresponding to lower field) with solid lines through the data to guide the eye. Selective incorporation of ^{77}Se isotopic labels in the clusters aids interpretation of the peaks. (a) A broad line near the shift of bulk CdSe is observed for interior labeled clusters. The major component of this line (at ~ 0 ppm) increases with increasing particle size. A sharp line in spectrum b is observed for clusters isotopically labeled in the selenium bonded to the organic ligands. This sharp resonance appears approximately midway between the shifts of CdSe and the next organoselenide materials. In spectrum c, the ^{111}Cd spectrum of the cluster also shows a broad line characteristic of the interior of the cluster. If present, an organocadmium signal would be upfield from zero ppm.

crystallite it does not redissolve on a competitive time scale). Experimentally there is no change in optical spectra if W is increased after growth is complete, showing that dissolution does not occur.

Importantly, this experiment suggests that a general "surface" chemistry may be performed on these colloidal crystallites. It has been reported that silylorganoselenides (e.g., RSeSiMe_3 , R = organic moiety) react quickly with metal salts to form metal-selenium covalent bonds.⁹ We now report that micelle stabilized CdSe crystallites having Cd-rich surfaces similarly react with PhSeTMS to give larger CdSe crystallites covered covalently with phenyl ligands (eq 1). The solution resulting from the stepwise



synthesis described above was treated first with an additional 0.06 mmol of Cd^{2+} to cover the crystallite surface with cadmium (trace 9). After a few seconds PhSeTMS (0.25 mmol in 16 mL of heptane) was added. This gave the precipitation of a red solid from the initially optically homogeneous, red colloid. The solid was separated from the supernatant by filtration (the filtrate being colorless) and washed exhaustively with petroleum ether and dried in air. The solid subsequently dissolved completely in pyridine.

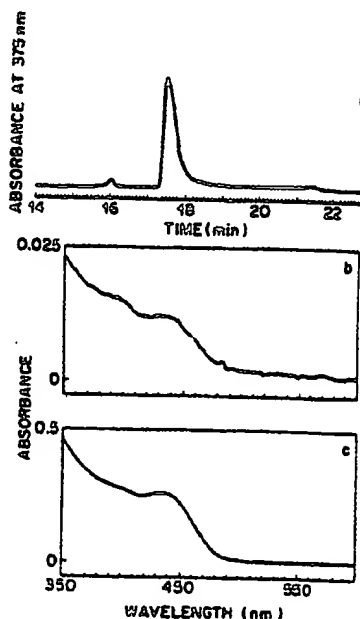


Figure 5. Size-exclusion chromatograms of "capped" CdSe clusters ($W \approx 0.9$). (a) Chromatographic trace (PL gel 500 column, pyridine mobile phase, 40°C) showing absorbance of the eluent at 375 nm versus retention time. The bulk of the material elutes as a single peak at 17.5 min. The small peak at $t = 16$ min represents CdSe cluster dimers, and the small peak at 21.5 min in Ph_2Se_2 . (b) UV-visible spectrum of the peak at 16.0 min. (c) UV-visible spectrum of the peak at 17.5 min.

giving a solution whose UV-vis spectrum is shown as trace g in Figure 3.

We propose that the solid is composed of CdSe crystallites with surfaces protected with phenyl ligands, based on the following evidence: (1) Electron micrographs of this "capped" material reprecipitated from pyridine are identical in structure with those of the surfactant-stabilized uncapped samples, showing crystallites of cubic CdSe. (2) The X-ray diffraction powder pattern (Figure 2) of the solid shows only broad peaks due to small zinc blende particles of CdSe. (3) ^{111}Cd NMR shows a broad peak (ca. 30 ppm upfield from bulk CdSe), and ^{77}Se NMR shows two non-overlapping regions of absorption: a sharp resonance (ca. 440 ppm downfield from CdSe) assigned to Se-Ph, and a broad resonance with partially resolved structure (ca. 50–100 ppm upfield from CdSe) assigned to Se atoms in small CdSe crystallites (Figure 4). (4) Far-infrared absorption spectra of a sample dissolved in a polystyrene film show a $\sim 190\text{-cm}^{-1}$ peak characteristic of the dipolar longitudinal optical mode of a spherical crystallite, and resonance Raman spectra show a $\sim 206\text{-cm}^{-1}$ peak characteristic of an internal longitudinal optical mode. Analyses of NMR¹⁰ and vibrational spectra are involved and will be reported separately. (5) Pyrolysis of a sample of the "capped" cluster yields bulk cubic CdSe as the only observed solid-state product, and Ph_2Se_2 as the primary organic products. (6) Size-exclusion chromatography of this material shows one major peak, and the UV-vis spectrum of the eluted peak is the same as that of the injected sample, this observation showing that there is essentially only one type of species in solution (Figure 5). All this evidence supports our conclusion that the solid is composed of surface-derivatized CdSe crystallites. The NMR evidence and our mechanistic discussion suggest that the phenyl group is bonded to a surface Se atom that is part of the sp^3 cluster network. We presently have no further evidence on surface reconstruction or bonding.

The phenyl capping reaction effectively changes the crystallite surface from hydrophilic to hydrophobic. The crystallites leave

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the water pump and then precipitate. The surfactant, cationic reagent, and other reaction products are easily removed as described. The hydrophobic cluster molecules obtained are unreactive in DMF, DMSO, or tetrahydrofuran (THF), and completely soluble in pyridine.

Conclusion

In this paper we have described two of our attempts of known macrocyclic solid electrolyte. The first is the use of bis(alkyl)chlorosulfate reagents in the anionic precipitation reaction. This has allowed for the fairly safe and convenient preparation of the electrolyte (both as solids and in bulk form) with liquid reagents. The second modification is more crucial. Using the controlled-growth ("living-polymer") process, culminating with the use of (organosilyl)chlorosulfates, we have been able to produce

the growing particles of the macrocyclic solid and thereby obtain molecular particles of the solid-state infinite lattice. These particles are molecular in both size (10-100 Å) and solubility.

The solubility of these materials has been critical to our study of them. Since the compounds are quite stable and since they dissolve so readily we have been able to begin their detailed characterization using many of the analytical techniques of solution-phase chemistry.

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MC-SCF Study of the Diels-Alder Reaction between Ethylene and Butadiene

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Abstract: In this paper we describe the results obtained in an MC-SCF STO-3G and 4-31G study of the cycloaddition reaction between butadiene (cis and trans) and ethylene. For this reaction it is possible to envisage three different mechanisms: a synchronous concerted approach, a nonsynchronous concerted approach, and a two-step process. At the STO-3G level we have found that the attack of ethylene on cis- or trans-butadiene involves three fragmentation transition states of diradicaloid nature associated with the syn-gauche, the trans, and the anti-gauche approach, which lead to three minima, again of diradicaloid nature, interconnected by two transition states of conformational origin. The attack on cis-butadiene involves also a fragmentation transition state of C₂ symmetry associated with the concerted synchronous attack, which, however, is disfavored on energy basis, and the preferred paths are those associated with the nonsynchronous approaches. The 4-31G results provide a completely different mechanism, which agrees well with the experimental evidence. The main differences are (i) the three fragmentation transition states seem to disappear, so that the region of the potential energy surface associated with the gauche and trans approaches becomes very flat, and (ii) the C₂ transition state is located at a slightly lower energy than the syn-gauche minimum. Therefore it appears that both synchronous and nonsynchronous paths exist and that the synchronous path is favored by ~2 kcal/mol.

1. Introduction

The Diels-Alder (DA) reaction is of great significance in the history of organic chemistry, from both an experimental and a theoretical point of view. However, despite the large number of experimental¹⁻⁴ and theoretical⁵⁻²² studies, the mechanism of

this reaction, even in the simple case of the reaction between butadiene and ethylene, is still in controversy. It is possible, in fact, to envisage three different mechanisms:²⁻⁵ (i) a synchronous concerted approach, involving a cyclic aromatic transition state (TS) with the two new C-C bonds formed to equal extent; (ii) a two-stage asynchronous concerted mechanism in which there are two distinct stages to changes in the bonding, some mainly between the reactants and the single TS and the others mainly between the TS and products; (iii) a two-step process, which occurs in two kinetically distinct steps via a stable diradical intermediate.

In this paper we limit our attention only to the simple Diels-Alder reaction between butadiene and ethylene. Experimentally,

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KIRK-OTHMER

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

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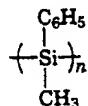
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silicon chain, giving rise to many interesting electronic properties (14,15). Because of this σ -conjugation, carrier transport along the silicon backbone is very efficient. The hole mobility of polysilanes, ca 10^{-4} cm²/V·s (16–19) is among the highest observed for polymers. Because the hole transport is through the σ -conjugated Si backbone, the hole mobility is insensitive to the substituent on the backbone. The hole mobilities of (phenylmethyl)polysilane (PMPS), poly(*n*-dodecylmethylsilane), poly(*n*-propylmethylsilane), and poly(methylcyclohexylsilane) are essentially the same (16,17). The charge generation efficiency and the spectral sensitivity range of polysilanes are, however, limited. Both can be enhanced by doping with sensitizers such as fullerenes (13).

Other polymers in this category include σ -conjugated polygermylenes (20) and π -conjugated polyacetylene, polythiophene, and poly(*p*-phenylenevinylene). The photoconductivity of many π -conjugated polymers can be enhanced by doping with fullerenes (21).

Liquid Crystalline Systems. Conventional photoconductive polymers are amorphous or systems with low order. In the case of PVK, the hole moves by hopping between the pendent carbazole groups. The hole mobilities are usually low, $\sim 10^{-6}$ cm²/V·s, due to a trap-dominated hopping transport (6–8). One approach to enhancing the hole mobility is to use conjugated polymers such as (phenylmethyl)polysilane (PMPS) (9–12). Another approach is the use of liquid crystalline systems where, in principle, transport can occur between ordered mesogenic groups (22–24).



The number of examples of liquid crystalline systems is limited. A simple discotic system, hexapentyloxytriphenylene (17) (Fig. 4), has been studied for its hole mobility (24). These molecules show a crystalline to mesophase transition at 69°C and a mesophase to isotropic phase transition at 122°C (25). In the mesophase, the molecules exist in a discotic hexagonal columnar ordered structure, schematically shown in Figure 4.

The ordered columnar arrangement of the hexapentyloxytriphenylene molecules provides good overlap of the *p*-electrons of the triphenylene moieties along the director axis. This results in efficient hole transport in the mesophase. The hole photocurrent shows nondispersive transport with a high mobility up to 1×10^{-3} cm²/V·s (24).

Nanoclusters/Polymer Composites. The principle for developing a new class of photoconductive materials, consisting of charge-transporting polymers such as PVK doped with semiconductor nanoclusters, sometimes called nanoparticles, Q-particles, or quantum dots, has been demonstrated (26,27).

The foundation for this new class of material is based on the ability to synthesize small semiconductor particles, typically in the nanometer-size regime (28–30). The structures of these semiconductor nanoclusters are usually the

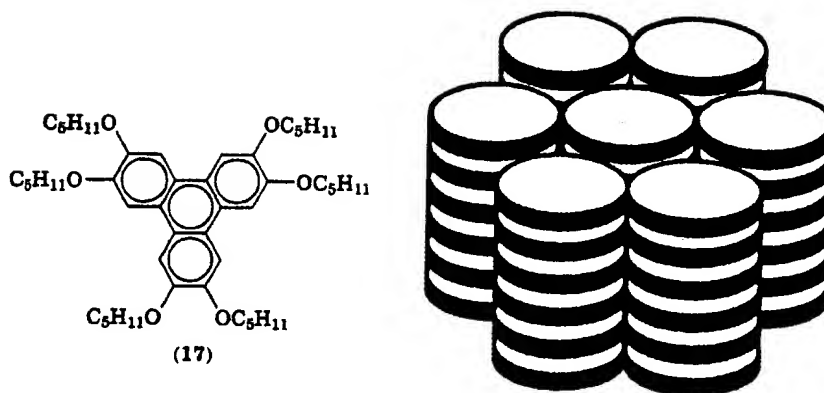


Fig. 4. Hexapentyloxytriphenylene (17) and a schematic view of its columnar mesophase (24).

same as those of the bulk crystals, yet their properties are remarkably different. The electronic properties of these clusters depend on the cluster size, a phenomenon commonly referred to as the quantum size effect (28,29). It is manifested as a blue-shift in the exciton energy and enhancement in the volume-normalized oscillator strength as the cluster size decreases. An exciton is an electron-hole pair bound by Coulomb interaction. With the proper surface-capping agents, clusters of varying sizes can be isolated as powders and redissolved into various organic solvents in the same manner as molecules. By co-dissolving these clusters with the polymer, a thin film of nanocluster-doped polymer can be easily made by spin-coating. Alternatively, semiconductor nanoclusters can be directly synthesized in the polymer film (26-30).

So far polymers such as PVK, polysilane, and amine-doped polycarbonate have been used as the charge-transporting matrices (26,27). A wide variety of semiconductor nanoclusters have been synthesized within these polymers (26,27). Many narrow gap and ir-sensitive semiconductors such as InAs normally cannot be made into high field, room temperature photoconductors for electrophotography purposes. Other than the typical difficulty of growing good quality large area thin film, the main problem is the dark decay owing to thermal excitation of carriers. By dispersing nanometer-sized InAs in charge-transporting polymers, the charge-generation efficiency of InAs is retained, but the dark decay problem is removed. An additional benefit is the ease of thin-film preparation with polymers.

This new class of photoconductive nanocluster/polymer composites have not been extensively characterized and much work remains to be done. For example, the doping of semiconductor nanoclusters was shown to enhance the charge-generation efficiency of the polymer, but the effects on the transport properties are not yet known. Inorganic semiconductors such as CdS, Si, and Se have much higher ($>10^{-1} \text{ cm}^2/\text{V}\cdot\text{s}$) carrier mobilities than organic polymers. Many of them are also electron-transport material, unlike polymers, which are usually hole-transport material. It is therefore of interest to examine the transport properties of composites containing small inorganic clusters embedded in polymers.

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Muscovite is found in regionally metamorphosed aluminous rocks that formed under a wide range of physical conditions. In igneous rocks, it occurs in some types of granites, in aplites, and as books in pegmatites. It is a characteristic phase of greisens which are produced when fluorine and other volatiles are introduced from granitic melts into adjacent rocks. Sericite is the name given to fine-grained white mica, usually muscovite. This mineral is a widespread gangue mineral in many hydrothermal ore deposits, either in the deposits themselves or in the adjacent altered wall rocks. Paragonite occurs in schists, gneisses, quartz veins, and fine-grained sediments. Phlogopite is a product of regional metamorphism of impure magnesian limestone. It is also characteristic of mantle-derived kimberlites and inclusions in kimberlites. Of all the micas, biotite occurs in the widest range of geological settings. It is common in the thermally metamorphosed rocks adjacent to granitic intrusions. In regionally metamorphosed rocks, it occurs in schists with chlorite, garnet, staurolite, kyanite, and sillimanite, although not all of these simultaneously. In plutonic igneous rocks, biotite is most common in intermediate and acid rocks, but it even occurs in some norites. Biotite books are found in pegmatites. Lepidolite is the most common lithium-bearing mineral and occurs almost exclusively in pegmatites with beryl, topaz, tourmaline, and other lithium minerals such as spodumene and amblygonite. It is also found occasionally in granites and aplites. *SEE APLITE; GRANITE; PEGMATITE.*

Uses. Commercial mica is of two main types: sheet, and scrap or flake. Sheet muscovite, mostly from pegmatites, is used as a dielectric in capacitors and vacuum tubes in electronic equipment. Lower-quality muscovite is used as an insulator in home electrical products such as hot plates, toasters, and irons. Scrap and flake mica is ground for use in coatings on roofing materials and waterproof fabrics, and in paint, wallpaper, joint cement, plastics, cosmetics, well drilling products, and a variety of agricultural products. *SEE CAPACITOR; ELECTRIC INSULATOR; SILICATE MINERALS.*

Lawrence Grossman

Mica schist

A widely distributed group of rocks of medium to high metamorphic grade, composed essentially of mica and quartz and exhibiting a foliated or schistose structure which is easily revealed by the parallel orientation of the mica flakes. Varieties are biotite schists, biotite-sericite schists, biotite-chlorite schists, and albite-biotite schists. Of lower metamorphic grade and of fine grain are phyllites or chlorite-sericite schists, without biotite but otherwise similar to mica schists, into which they pass by gradual transitions. *SEE MICA; PHYLLITE; QUARTZ.*

The simple mineral composition of the ordinary mica schist (quartz and micas with or without feldspars) demonstrates the rule of the paucity of mineral phases. Micas are members of a chemically complex mineral group, and during the metamorphism and the crystalloblastic growth of mica, all possible ions try to accommodate themselves in its crystalline structure: those that cannot be simply carried away. However, this process cannot go on indefinitely. Eventually the composition is overstrained and if, for

example, the alumina concentration is high, new minerals like andalusite, sillimanite, cordierite, or almandine garnet may develop. Rare types contain corundum, paragonite, and fuchsite. Minor accessories are rutile, zircon, tourmaline, and iron ores. When feldspar minerals are abundant, mica schist grades into gneiss; with an increase of quartz it grades into micaceous quartzite.

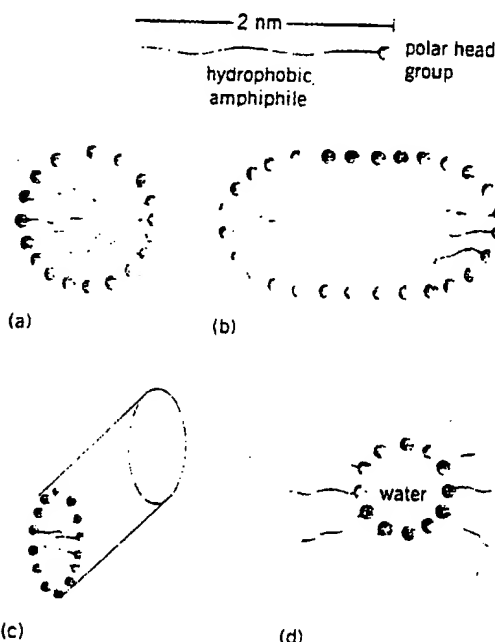
Mica schists are most widely distributed in Precambrian areas and in the younger eroded mountain ranges where they usually represent metamorphic equivalents of aluminum-rich sediments (clays and argillites). However, tuffs and certain acid igneous rocks (rhyolites, granites) may form part of the primary constituents. Contrary to earlier belief, metasomatic alterations are insignificant; the chemistry is conservative and reflects rather well the original composition. *SEE METAMORPHIC ROCKS.*

T. F. W. Barth

Micelle

A colloidal aggregate of a unique number (50 to 100) of amphipathic molecules, which occurs at a well-defined concentration called the critical micelle concentration. In polar media such as water, the hydrophobic part of the amphiphiles forming the micelle tends to locate away from the polar phase while the polar parts of the molecule (head groups) tend to locate at the polar micelle solvent interface.

A micelle may take several forms, depending on the conditions and composition of the system, such as distorted spheres, disks, or rods (illus. a, b, and c). The dimensions of the particle are derived from those of the amphiphile, for example, a sphere radius of about 2 nanometers or a rod cross-sectional radius of 2 nanometers. Frequently the polar head group is a salt which ionizes in polar media. The micelle may have about 30% of the amphiphiles in the ionized state, giving rise to a highly charged particle surrounded by a cloud of counterions (ions with a charge



Form of an amphiphile and several forms of micelle: (a) spherical, (b) disk, (c) rod, and (d) reversed.

opposite to that of the micelle ions), and also counterions bound into the micelle surface. Micelles are formed in nonpolar media such as benzene, where the amphiphiles cluster around small water droplets in the system, forming an assembly known as a reversed micelle (illus. d).

When the surfactant contains two long alkyl chains, a vesicle structure rather than a micelle is formed because of geometric restraints. This entity consists of two closed concentric spherical layers of surfactant which enclose an internal volume of water. Such a structure is similar to that of a biological membrane; micelles and vesicles mimic biological systems both in structure and in many kinetic processes. *SEE CELL MEMBRANES.*

Micellar systems have the unique property of being able to solubilize both hydrophobic and hydrophilic compounds. They are used extensively in industry for detergency and as solubilizing agents. A strong catalytic action is often associated with these systems and is attributed to the clustering of reactants in the micelle, thereby creating high local reactant concentration, and also to the strongly charged surface which influences the transition state of a reaction. *SEE DETERGENT; SURFACTANT.*

The locally high concentration of guest molecules or reactants in a micelle surface leads to enhanced rates of reaction over those observed when the reactants are dispersed in the bulk phase. This catalytic effect can be as large as 1000-fold and can, in some cases, be used selectively. Photolysis of dialkyl ketones in micelles leads to radicals whose local concentrations are high. Only a portion of these radicals can react in micelles, those that have experienced spin relaxation due to their particular isotopic constituency. The unreacted portion with a different isotopic constituency diffuse into the bulk phase and give alternative products. The technique has been used successfully to produce isotopic enrichment. *SEE CATALYSIS; FREE RADICAL.*

Micelles play an important role in photo-induced reactions, in particular photo-induced electron transfer reactions. Anionic micelles such as sodium dodecyl sulfate strongly promote photoionization of several molecules (for example, phenothiazine, aminopyrene, or tetramethyl benzidine) located at the micelle interface. The ionization threshold is reduced by more than 3.0 eV (>70 kilocalories (300 kilojoules) per mole), an effect not observed in homogeneous solution. The electron of the guest molecule is transferred to the aqueous phase and observed as a hydrated electron, while the cation is stabilized by the micelle. Electron transfer between two guest molecules, giving two radical ions, often occurs most efficiently on micellar systems. The high local concentration and the interface promote electron transfer and lead to efficient reaction. The charged micelle interface stabilizes the ion of opposite charge, while repelling into the bulk water phase the ion of like charge. This latter effect of the micelle surface leads both to efficient charge separation and to long-lived radical ions. The ions can be used to generate useful chemistry via subsequent reaction with other components of the system. In particular, the presence of catalysts such as colloidal platinum can lead to water breakdown, the radical anion donating an electron to the platinum which leads to the formation of hydrogen. These types of micelle-mediated processes are of use in the storage of solar energy. *SEE PHOTOCHEMISTRY.*

J. K. Thomas

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Microbial biofilm

An adhesive substance, the glycocalyx, and the bacterial community which it envelops at the interface of a liquid and a surface. When a liquid is in contact with an inert surface, any bacteria within the liquid are attracted to the surface and adhere to it. In this process the bacteria produce the glycocalyx. The bacterial inhabitants within this microenvironment benefit as the biofilm concentrates nutrients from the liquid phase. However, these activities may damage the surface, impair its efficiency, or develop within the biofilm a pathogenic community that may damage the associated environment. Microbial fouling or biofouling are the terms applied to these actual or potential undesirable consequences.

Microbial fouling affects a large variety of surfaces under various conditions. Microbial biofilms may form wherever bacteria can survive; familiar examples are dental plaque and tooth decay. Dental plaque is an accumulation of bacteria, mainly streptococci, from saliva. The attachment of bacteria to the tooth is not random. Certain types of bacteria are specific to certain locations on the tooth: anaerobic bacteria are found deep within the biofilm, whereas aerobes are found near the plaque-air interface. The ability of the biofilm to concentrate nutrients is not important in this environment because the mouth itself is rich in nutrients; rather, the plaque protects the inhabitants from being transported by swallowing to a more hostile environment in the stomach. The process of tooth decay begins with the bacteria colonizing fissures in and contact points between the teeth. Dietary sucrose is utilized by the bacteria to form extracellular glucans that make up the glycocalyx and assist adhesion to the tooth. Within this microbial biofilm or plaque the metabolic by-products of the bacterial inhabitants are trapped; these include acids that destroy the tooth enamel, dentin, or cementum. *SEE PERIODONTAL DISEASE; TOOTH DISORDERS.*

Nature and formation. The formation of a biofilm commences with the transportation of bacteria from the liquid phase to a contiguous surface. The mechanisms involved are sedimentation, chemotaxis, Brownian motion, cell surface hydrophobicity, and fluid dynamic forces. A hypothesis explaining the process of attraction postulates that different combinations of force affect the bacteria according to their distance from the surface. Van der Waals forces operate at a distance greater than 50 nanometers from the surface and give a rapid but weak attraction; both van der Waals and electrostatic interactions occur together between 10 and 20 nm from the surface. At a distance of less than 1.5 nm from the surface, van der Waals forces, electrostatic interactions, and specific interactions occur, producing an irreversible binding between the bacteria and the surface. This binding is associated, in some instances, with the production by the bacteria of adhesive materials, such as exopolysaccharides, that form the glycocalyx. Not all of the different adhesive media are known. Many factors affect the initial colonization of the surface, including surface roughness, the nature of the surface, the ve

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